TITLE:

Injection of coal fly ash slurry in deep saline formations for improved CO_2 confinement – A theoretical concept

HIGHLIGHTS:

- We discuss a theoretical concept for improved CO_2 confinement in saline formations.
- The concept involves the injection of fly ash slurry and CO_2 in separate wells.
- CO_2 combined to mineral slurries injection causes pressure build-up.
- This pressure build-up could be managed by extracting formation brine.
- The technological feasibility of the concept is not addressed here.

Injection of coal fly ash slurry in deep saline formations for improved CO_2 confinement – A theoretical concept

F.J. Doucet[a]*, *T.K. Mlambo*[a], *E.M. van der Merwe*[b], *W. Altermann*[c]

[a] Mineral Waste Beneficiation Group, Council for Geoscience, Private Bag X112, Pretoria 0001, South Africa.

[b] Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa.

[c] Department of Geology, University of Pretoria, Pretoria 0002, South Africa.

* Corresponding author: fdoucet@geoscience.org.za; +27 12 841 1300

Abstract

98% of South Africa's total CO_2 geological storage capacity is in the form of deep saline formations located off-shore, while the remaining 2% is situated on-shore. Such formations may not have a similar proven sealing capacity to that of depleted gas and oil reservoirs, and the country must give due consideration to every theoretically conceivable option for CO_2 storage. This paper discusses a theoretical concept whereby coal fly ash slurries, composed of homogeneously-sized ultra-fine particles with adequate shear-thinning Newtonian rheological properties when suspended in water, could be injected in deep saline formations, alongside CO_2, to engineer a 'mineral curtain' that could act as a barrier preventing unwanted CO_2 migration outside the boundary layers of the reservoir. The resulting pressure build-up could be managed

by extracting the brine from the formations, which could then be used to produce fresh water for local communities deprived of drinking water.

Keywords: fly ash; carbon dioxide; geological storage; saline formations; brine extraction

1. Introduction

Carbon capture and storage (CCS) involves the separation of carbon dioxide (CO_2) from industrial and energy-related sources, its transport to a suitable location, and its long-term storage distant from the atmosphere. The most advocated storage method involves storing CO_2 in dense, supercritical liquid form into pore spaces in deep underground geologic formations. A critical aspect of geosequestration is the existence of suitable high-integrity geologic sites for the safe, long-term storage of CO_2. Deep formations containing saline brines offer the highest potential CO_2 storage capacity [1], and this is also the case for South Africa where the estimated maximum geological storage capacity is around 150 Gt of CO_2 [2].

Unlike depleted hydrocarbon reservoirs which are historically proven to be well-confined, saline formations may not have a similar proven sealing capacity. Such formations are very often open, allowing for some lateral displacement of the formation water beneath the caprock. The velocity of this flow will increase during CO_2 injection and will ultimately be dictated by the backpressure imposed by the formation water onto CO_2 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_2, which at reservoir conditions (*i.e.* below 800m) will be in the supercritical state (sc-CO_2) [3]. The CO_2-supplemented formation will host a myriad of intricate dissolution and precipitation reactions. These chemical and physical effects of CO_2 injection will strongly depend on the types of minerals forming the host environment and on the pore fluids. Therefore, the equilibrium between the lithostatic pressure and the pore pressure will be changed upon CO_2 injection, and together with the *in situ* mineral dissolution and precipitation processes, these occurrences may have a strong bearing on the permeability of the reservoir and the sealing capacity of the formation. Understanding the reactivity of the storage reservoir rock (*e.g.* sandstone) in saline formations with injected CO_2 is essential to predict the short-, medium and long-term fate of CO_2. Whilst significant effort has been made to better comprehend CO_2 mineralization via carbonate precipitation [4], a lesser amount of information is available on rock-brine-CO_2 interactions following CO_2 injection. It is however known that, depending on the nature of the interactions, they may either cause (1) increased porosity and permeability [5] and (1.a) subsequent greater storage capacity of the intended reservoir, or (1.b) unwanted CO_2 migration outside the boundary layers of the reservoir, or (2) decreased porosity and permeability with reduced injectivity due to mineralization [4]. Details on competing geochemical processes were discussed elsewhere [6,7], but it is evident that some of these processes may alter the integrity of deep saline formations and thereby disrupt the safe, long-term storage of CO_2. Saline formations can also contain fault zones which may act as conduits for fluid flow. The potential of injected CO_2 or the resulting pressure front to encounter a fault is real, with probabilities of up to 20% having been recently estimated [8]. The potential for CO_2 and/or brine leakage outside the confining boundaries of the target formations is therefore an area of considerable uncertainty for the geological storage of CO_2 [9].

Some insightful experience has already been gained from past and existing pilot and commercial projects around the world [10]. Issues that have been identified include the need (i) to consider multiple injection wells, (ii) to optimize the usage of storage space, and (iii) to assess and quantify the potential impact of large CO_2 injection volumes on the quality and movement of formation water. The theoretical concept addressed in this communication encompasses all three of these issues.

A calcium- and/or magnesium-rich slurry could be injected at strategic locations in deep saline formations [11]. The purpose of this injection strategy would be to prevent the unwanted migration of injected CO_2 plumes beyond the confining layers of the formations via induced, accelerated and localized underground mineral carbonation. The object of this paper is two-fold: (i) to highlight some perspectives on this concept without addressing its technological feasibility, and (ii) to extent the discussion to the possibility of using coal-combustion fly ash as the basis for the injection slurry. Such injection strategy could also be combined with the recently proposed Active CO_2 Reservoir Management strategy [12].

2. Improved integrity of saline formations

2.1. Background of concept

The injection of reactive mineral slurries at strategic sites of deep saline formations may help prevent the migration of CO_2 plumes beyond their confining layers via localized underground mineral carbonation. Researchers from the Albany Research Centre (USA) have previously suggested this possibility of co-injecting ultramafic mineral slurries (*e.g.* olivine, serpentine) with CO_2 in such geologic media, and reflected on several conceivable scenarios [11]. The research team has since shifted its focus on ‘conventional’ geological sequestration in depleted oil and gas reservoirs or deep saline formations with a thick, impermeable caprock (O’Connor, personal communication), given that numerous large reservoirs for CO_2 sequestration are available in the USA. South Africa, on the other hand, is not well-endowed with natural worldclass reservoirs for geosequestration, such as oil- and gas-depleted reservoirs which have proven to be capable of storing fluids and gasses for millions of years. It relies heavily on deep saline formations for its CCS endeavor [2] and it must therefore give due consideration to every theoretically conceivable option for CO_2 storage.

The injection of mineral slurries made up of olivine or serpentine is not an attractive option in South Africa. A possible alternative material may be in the form of tailings from platinum and diamond mines. For instance, Platinum-Group Metals (PGM) tailings are readily-available, with about 77-million tons of Merensky, UG2 and Platreef tailings generated annually in South Africa [13]. They are fairly rich in magnesium (Mg)- and calcium (Ca)-containing minerals (plagioclase, olivine, orthopyroxene, clinopyroxene) and have already undergone ultrafine grinding ($D(v,50) < 66$ µm) in order to liberate the valuable PGM commodities from the host rock which are typically less than 30 µm in size [14]. However, this application for PGM and diamond tailings is unlikely to receive support from the respective industries which continuously attempt to extract additional economic commodities from their tailings through beneficiation processes. Given South Africa's history of intensive mining, a possible alternative material may therefore be in the form of magnesium-rich mine tailings from the Bushveld Complex or the Kimberley area. However, this application for tailings is unlikely to receive support from the mining sector, which continuously attempts to beneficiate their stock piles. Coal fly ash (FA) may represent a more suitable alternative to ultramafic minerals.

2.2. Case for the use of fly ash

The worldwide production of FA approximates 660 million metric tons. In South Africa, only *ca.* 5% of the FA generated by coal-fired power stations is currently reused [15]. Hundreds of Mt of fresh and dumped FA is therefore readily-available at low cost. FA has a mineral structure which is more reactive than primary minerals. It can be classified into homogeneously-sized and very fine (*e.g.* sub-10 µm) particulate materials with adequate rheological properties (shear-thinning and Newtonian; [16]). The latter property is important since the injection of FA slurries in the porous rocks would only be possible if the integrated network of intergranular voids can accommodate the size of the particles forming the mineral slurries and their rheological properties without premature clogging. While the carbonation of FA has already been demonstrated under subcritical CO_2 conditions [17], it may not occur in brine water under sc-CO_2 conditions such as those found at deep geological depths. Our group is currently demonstrating the reactivity of FA with sc-CO_2 in brines.

2.3. Conceptual injection strategies

Three distinct scenarios for the injection of CO_2 and mineral slurries were previously discussed [11], although not all of them are favorable.

The first scenario involves the simultaneous co-injection of the mineral slurry and CO_2 through a single primary injection well. Such an injection approach may help envelope the CO_2 plume with an "engineered carbonate curtain" and thereof prevent the uncontrolled diffusion of CO_2 outside the saline formation [11]. However, this scenario is likely to cause premature clogging of the pore spaces by the mineral slurry and the newly-formed mineral carbonates at proximity of the injection well. This would subsequently prevent further CO_2 injection. Although the economic advantage of using a single well for the injection of the two materials is apparent, it is also clear that this strategy is not conceivable.

A variation to this first scenario is the injection of CO_2 at a primary well and that of the mineral slurry at one or several secondary wells. This approach gives the option of placing mineral slurry walls at strategic locations around the CO_2 plume, in existing fractures, or between CO_2 and fault zones or facies changes. This helps prevent premature clogging and carbonate precipitation at the primary injection well, but it requires additional costs for the construction of secondary injection wells. Key to this scenario will be the selection of appropriate locations and depths of the wells with regard to zones of faults or fractures within the target formation, the appropriate well spacing, and the appropriate concentration of mineral reactant to inject into the secondary wells. This exercise would require an extremely detailed knowledge of the lateral and vertical distribution of mineralogy and porosity of the storage horizons and the sites of possible zones of weakness of the geological seals.

The third application entails filling minor faults in overlaying caprocks with mineral slurries. This would ensure vertical isolation of the CO_2 plume through minimization or prevention of the risk of leakage through the caprock [11]. Pressure build-up would however be considerable, CO_2 injectivity would be challenging and the excess pressure may cause increased risk of leakage. A key aspect of all CCS options is the sealing efficiency of caprocks above potential CO_2 storage reservoirs. A real, continuous and ubiquitous CO_2 migration process in the form of diffusive loss of CO_2 through pore spaces of the caprock [18] or by upward capillary percolation due to the re-activation of micro-fractures in the caprock [19] is generally accepted. However, rapid leaching by seal-breaching would represent an unacceptable threat in the case of fracture-filled overlaying caprocks.

The most conceivable application of induced localized mineral carbonation to CO_2 geological sequestration is therefore offered by the possibility of engineering a “mineral curtain” which will over time undergo some degrees of carbonation and ultimately form a “carbonate curtain”. The curtain must be placed between the primary injection site of CO_2 and potential weakness points (i.e. fault zones, fractures, facies changes) in the target formation where CO_2 could migrate towards and across with subsequent rapid leakage outside the borders of the formation. The “carbonate curtain” would form from the volume expansion occurring upon carbonate formation, which would fill the pore spaces between the formation grains, and would thereby act as a barrier preventing the injected CO_2 to migrate further towards the aforementioned weakness points.

How efficient the so-formed mineral and subsequently carbonation curtain will be in preventing CO_2 migration is unsure at this stage. The feasibility of the proposed concept will also depend on the impact of injected mineral slurries on CO_2 injectivity, pressure build-up and risk of induced seismicity, the mechanisms and kinetics of formation and the structural properties of the carbonated curtain, and on the range of geochemical changes induced by the co-injection strategy in the target geological formations.

2.4. Combining CO_2 injection with mineral slurries injection and water production

A significant pressure increase due to CO_2 combined to mineral slurries injection represents an obvious limiting factor in storage capacity. This pressure build-up could however be managed by extracting the resident brine from saline formations, which would also reduce the risk of CO_2 and brine migration [12]. In its natural state, deep saline formations contain little CO_2 in comparison to the volumes of CO_2 injected during geological sequestration. Upon CO_2 injection the brine contained in formations will migrate and be subsequently extracted before injected CO_2 comes into contact with it. It is therefore unlikely that any significant amount of injected CO_2 would return to the surface during brine extraction. An added benefit for South Africa, which is classified as a semi-arid country, is that extracted brine could be used to produce fresh water via desalination [12], which can then be supplied to local communities deprived of drinking water. Extracted brine could also be treated as a source of marketable products (*e.g.* geothermal energy in the form of recovered heat; minerals; saline water for cooling towers) [20]. However, the technical feasibility of brine management, expressed in terms of costs, benefits and environmental impacts, depends strongly on regional factors such as climate and aquifer parameters [21].

3. Conclusion

The strategic injection of fly ash-based mineral slurries may prove to be an effective tool to form 'man-made' seals in saline formations. While this theoretical concept may be conceivable, numerous challenges need to be overcome before the proposed scenario can become technologically feasible for the safe, long-term geo-sequestration of CO_2 in such environments.

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