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MINERALISATION – CARBONATION AND ENHANCED WEATHERING

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This report describes research sponsored by IEAGHG. This report was prepared by:

Steve Goldthorpe

The principal researchers were:

- Aameena Camps
- Steve Goldthorpe
- Matt Green

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The IEAGHG manager for this report was:

Tim Dixon

The report should be cited in literature as follows:

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Further information or copies of the report can be obtained by contacting IEAGHG at:

IEAGHG, Orchard Business Centre,
Stoke Orchard, Cheltenham,
GLOS., GL52 7RZ, UK
Tel: +44(0) 1242 680753 Fax: +44 (0)1242 680758
E-mail: mail@ieaghg.org
Internet: www.ieaghg.org

Mineralisation – carbonation and enhanced weathering

Executive Summary

This technical review is an update of a 2005 IEAGHG review of mineralisation as means of CO₂ sequestration, which concluded “*Significant breakthroughs are needed but obstacles to be overcome are considerable*”. This review confirms that view and concludes that recent research initiatives are unlikely to lead to technically and economically viable CO₂ sequestration processes.

An insurmountable barrier is the scale of mineral handling that would be required for CO₂ absorption by a mineral at a coal-fired power station. The amount of igneous mineral material to be mined, processed and returned to the ground would involve materials handling at an order of magnitude greater scale than the scale of the coal mining operation that provided the fuel that is burned to produce the CO₂. That would result in significant environmental consequences and life-cycle energy demands.

Natural carbonation of minerals is a very slow process that would need to be greatly accelerated to provide a useful industrial process. The recent research initiatives have focussed on complex processes, involving staged conversion at high temperature and high pressure and conditions. Catalysis also requires acidic conditions. Technically attractive concepts have not yet been defined, so these ideas have not advanced to the stage of requiring assessment of economic viability.

An alternative mineralisation concept is the spreading of alkaline minerals on the ground for the purpose of drawing down CO₂ from the atmosphere via enhanced mineralisation. This review has identified that there is a wide divergence of views on the optimum particle size for material to perform that function. This geo-engineering approach to addressing climate change is probably limited to situations where there is a beneficial side-effect of infrastructure projects.

In summary, no technology breakthroughs have been identified in this review of mineralisation concepts.

This review was prepared by Steve Goldthorpe for IEAGHG.

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1. Introduction

Carbon dioxide capture and storage technology (CCS) involves the separation of CO₂ from flue gases and storage of that CO₂ underground. For CCS to be effective as a remedy for climate change, it is essential that the CO₂ is sequestered in perpetuity. There is concern that trapping CO₂ in depleted hydrocarbon fields or deep saline aquifers may not be permanent. Therefore there is interest in alternative schemes involving chemically fixing CO₂ into rocks in the form of carbonates.

Igneous¹ rocks containing high quantities of calcium and magnesium silicates, such as peridotite and basalt, react with CO₂ in the atmosphere to produce carbonates during the natural very slow weathering processes. Mimicking and greatly accelerating that natural process is the aim of a branch of CCS research called mineralisation with the aim of creating a permanent, stable and environmentally safe way of storing carbon.

Three areas of research into mineralisation of CO₂ have been pursued.

- In-situ mineralisation, whereby injected CO₂ reacts with an igneous rock formation, typically basalt, to fix it as carbonates. The status of research on in-situ mineralisation has been recently addressed by IEAGHG in 2011/TR2 *Geological storage of CO₂ in basalts*.
- Surface mineralisation or enhanced weathering, whereby natural silicates, or CO₂ absorbing waste materials, are spread on the ground with a view to drawing down CO₂ from the atmosphere. This concept is discussed in this report.
- Ex-situ mineralisation, whereby a source of silicate material (feedstock) is transported to a location for reacting with captured pure CO₂ before being returned to a permanent storage location.

A wide ranging study of potential process routes for ex-situ mineralisation was examined in IEAGHG (2000). A subsequent review was carried out by ECN (IEAGHG 2005). That later report found that many of the processes identified in the earlier scoping report were no longer under consideration and concluded *“There has been a shift to investigate other mineral carbonation processes since the IEAGHG 2000 report as researchers look for an economically viable route. Research is still active but in a relatively small number of institutions. Significant breakthroughs are needed but obstacles to be overcome are considerable. However, the raw materials required for mineral carbonation are globally abundant and this potential makes further research attractive. A watching brief should be kept for significant advances in mineral carbonation.”*

In this review the process challenges of in-situ mineralisation are discussed and some recent papers are reviewed describing work to address those challenges in the search for significant breakthroughs.

¹ Igneous rocks, such as peridotite and basalt, are derived from magma or lava that had flowed to the surface and cooled, as distinct from sedimentary or metamorphic rocks derived from the deposition of weathered mineral material.

2. Surface Mineralisation

Surface mineralisation, often referred to as enhanced weathering, is the acceleration of the natural process by increasing the surface area of the rocks in an attempt to draw down CO₂ directly from the atmosphere.

In his masters thesis, Ernes (2010) evaluates a potential practical implementation of enhanced weathering based on the use of olivine as a gravel road building substitute in Mozambique. Ernes estimates CO₂ absorption costs for mining, grinding and transport in the range \$13-\$65 per tonne of CO₂ sequestered. Key variable parameters are the distance of transport from the mine to the application and the extent of grinding of olivine. A potential limitation of this scenario is olivine dissolution in rainwater. His analysis is based on the road surface lasting for 20 years.

An unpublished environmental lifecycle analysis (Koornneet and Nieuwlaar, 2009) reviews a range of environmental issues with enhanced weathering of olivine and concludes that a conceptual application on the Dutch coast scores well in comparison with conventional CCS. In contrast, an assessment of spreading crushed olivine on beaches by Hangx & Spiers (2009) concludes that coastal spreading of olivine is not a viable method of CO₂ sequestration on the scale needed.

Hangx & Spiers (2009) Note that “*To obtain useful, steady state CO₂ uptake rates within 15–20 years requires grain sizes <10 μm.*”, whereas, Koornneet and Nieuwlaar report a range of 10-100 μm, as shown in Figure 1, based on a theoretical model.

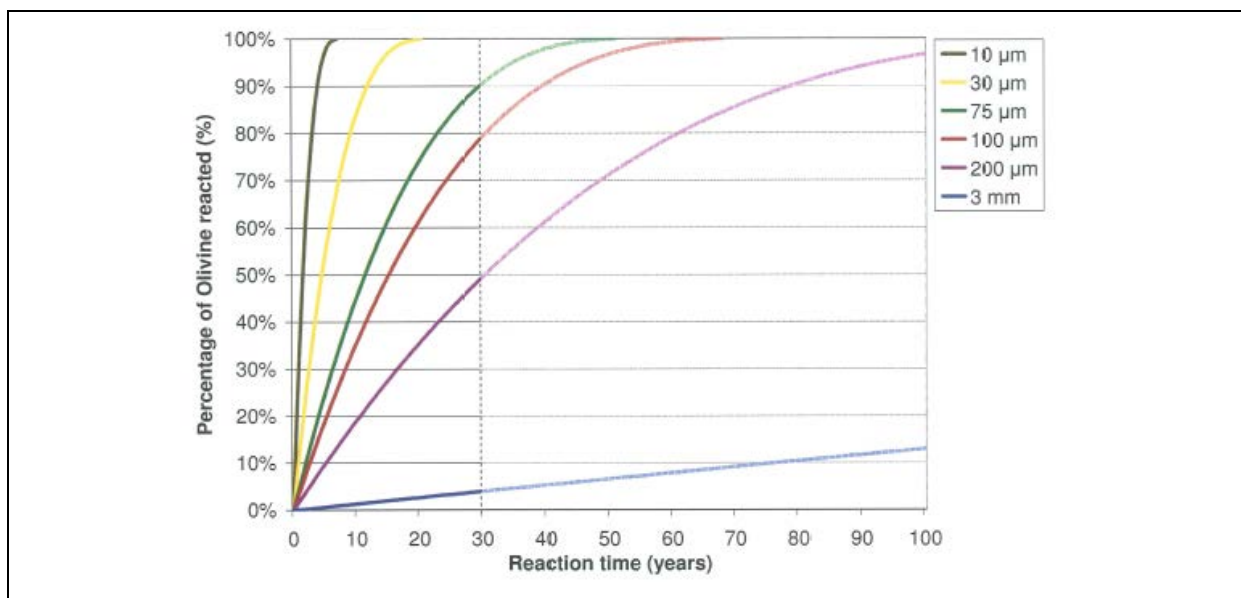


Figure 1 Relationships between particle size and progress of reaction for olivine (Koornneet and Nieuwlaar, 2009)

Ernes based his analysis on olivine particle sizes of 75, 425 and 2360 μm. It appears that there is a significant gap in the agreed understanding of the rate of reaction of crushed olivine with atmospheric CO₂.

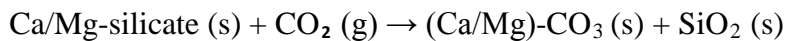
In addition to enhanced weathering of natural minerals, such as olivine, the surface spreading concept can be applied to the potential draw down of CO₂ by fly ash, or slag from iron making, on brown field industrial sites. However, the opportunities for such beneficial side effects of site preparation schemes would be site specific and very minor in a global context. A parallel process of draw down of atmospheric CO₂ by man-made minerals is the slow absorption of atmospheric CO₂ in the maturing and weathering of concrete.

Surface mineralisation, i.e. drawing down CO₂ from the atmosphere, is not directly related to fossil fuel combustion activity, but could be considered as a geo-engineering approach to solving the climate change problem. The scope for surface mineralisation is inherently constrained by land resources. Therefore this concept is limited to situations where it is a beneficial side effect of infrastructure projects.

3. Processes

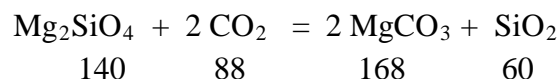
3.1 Direct ex-situ gas-solid carbonation

Gas to solid carbonation is the simplest approach to mineralisation, where gaseous CO₂ reacts with a solid silicate (typically magnesium or calcium² based) to form a carbonate as well as other secondary minerals, such as silicon dioxide (silica) according to the following generalised equation for the reaction: -



The major advantage of dry carbonation over enhanced weathering is the potential to harness exothermic energy produced when the reaction is conducted in an ex-situ environment with pure CO₂. However, both field and experimental evidence suggests that the rate-limiting step in CO₂ fixation by gas-solid carbonation is the release of cations from silicate minerals (Gislason et al, 2010). The reaction can be accelerated by pre-treating the mineral feedstock and by grinding it before use to increase the reactive surface area, but pre-treatment is very energy intensive.

Another significant concern is the scale of materials handling involved. In the case of magnesium silicate reacting with CO₂ to produce magnesium carbonate and silica the mass of pure olivine reacting is 1.59 times the mass of CO₂ absorbed.



In the case of a raw coal with 68% carbon content, the mass of pure olivine would be 4 times the mass of coal burned that produced the CO₂. In olivine some of the magnesium ions are substituted with heavier iron ions. Other minerals, such as serpentine and wollastonite, with

² Magnesium (atomic weight 24) is a better basis for mineralisation than Calcium (atomic weight 40) because the minerals are lighter. Otherwise the chemistry is the same.

capacity to react with CO₂, have a lower wt/wt absorption capacity than olivine. When incomplete reaction, mineral hydration and impurity of natural mineral deposits are taken into account, the mineral mining activity is likely to be an order of magnitude greater than the corresponding coal mining activity. The materials handling consequences of large scale mineral mining would add life cycle energy consumption considerations.

Also in this simplest dry form, the reaction is far too slow to be effective in CCS on a wide scale basis (Bonfils et al, 2012). This has led to aqueous mineral carbonation being a focal point of research.

3.2 *Ex-situ Aqueous Carbonation*

The addition of water to the direct carbonation process would significantly increase the rate of reaction, as can be seen when looking at the effect of rain in the natural weathering process, because of the mobilisation of ions in the reaction of carbonic acid with alkaline minerals. In the case of ex-situ aqueous carbonisation, the energy and economic cost needed for crushing and slurring the feedstock need to be offset by the carbonation process exotherm in order to make the process potentially viable on in the industrial context. Also to be considered when feedstock needs to be mined and processed at large scale, are knock on environmental effects that could be caused by the process.

No practical schemes for adequately enhancing ex-situ dry mineralisation processes by the addition of water have been identified in this review.

3.3 *Indirect Ex-situ Gas/solid Carbonation*

Carbonation has recently been investigated using a process route in which the silicates are first converted into hydroxides. This process consists of 3 steps.

1. Concentrating hydrated magnesium silicates from serpentinite³ (or other high Mg bearing rock)
2. Converting hydrated magnesium silicate into magnesium hydroxide
3. Reacting magnesium hydroxide with CO₂ to give stable magnesium carbonate

The conversion of silicates to hydroxides is endothermic, requiring the concentrated source rock to be heated to 500°C along with ammonium sulphate. The ammonium sulphate can be recovered and reused. Although the process of making the hydroxide requires heat, the carbonation reaction is exothermic, so some of that energy can potentially be recovered, offsetting some of the energy required in the hydroxide production process (Fagerlund and Zevenhoven, 2011). Further research has identified that energy and chemical costs can be reduced by carrying out the hydroxide/CO₂ reaction at high pressure and high temperature (25 bar; 450°C) potentially making the hydroxide route technically achievable on an industrial scale (Nduagu et al, 2012).

³ Serpentinite is a naturally occurring rock with a predominance of serpentine (Mg₂Si₂O₅(OH)₄) minerals.

However, as with direct carbonation, the scale of operations would be daunting. The amount of pure serpentine required to sequester CO₂ from a coal combustion flue gas via perfect chemical conversions would be about 5.4 times the amount of coal burned. With real mineral serpentine and practical reaction yields the amount of mineral mined for CO₂ capture purposes could be an order of magnitude greater than the amount of coal mined that resulted in the production of that CO₂. Similarly, the scale of thermal processing of the mineral to the hydroxide, and the high temperature carbonation process would require energy transfer equipment on a scale to rival the host coal combustion process.

4. Sources of Rock as Feedstock

The most appropriate source rocks are widely agreed to be silicates of calcium or magnesium. Other potentially suitable cations, such as iron, copper and zinc could also be used, but due to a high economic value of such silicate minerals, these are considered an unattractive prospect. The magnesium based minerals are predominantly sourced from olivine and serpentine and wollastonite is a corresponding calcium based mineral⁴. Basalt is usually a plentiful source of these minerals. Although basalt is effective for in-situ storage, where it could potentially be utilised in large quantities, it is ineffective for ex-situ industrial use. This is due to the large tonnage that would be needed compared to more pure deposits of minerals.

As noted above, the mining of feedstock for use in ex-situ carbonation would be very energy intensive, and could have wide environmental impacts. The mining of silicates as feedstock for CO₂ capture on coal fired power stations would greatly exceed the extraction of the coal itself (Kelly et al, 2011). Before being used, the mined silicates would also need to be treated, at least by being ground down to increase the reactive surface area. This is a very energy intensive process, with the feedstock typically needing to be ground as fine as 90µm (Prigiobbe and Mazzotti, 2011).

Industrial waste can be considered for use as source of feedstock. Metal slag and fly ash were assessed by Kelly et al (2011), who found that metal slag required energy intensive processing that made it non-viable as a sink for CO₂, but fine fly ash was more promising. Carbonation of waste materials could give benefits in making alkaline slag or fly ash more benign if it is to be land-filled (Li et al. 2007). Conversely, if the alkaline properties of such materials are to be used beneficially, e.g. in applications such as cement additives, then neutralisation of the fly ash by carbonation would be counter-productive.

By using coal fly ash as a feedstock for carbonation, it has been suggested that part of the CO₂ produced during the combustion process that created it might be offset. The feedstock is already close at hand and very fine, with low costs for extraction and transportation. Experiments by Bauer et al (2011) suggest that with lignite fly ash, there was a high CO₂ uptake, with a carbonation rate of 53% in 120 minutes. However, the CO₂ absorption

⁴ Olivine = Mg₂SiO₄; Serpentine = Mg₃Si₂O₅(OH)₄; Wollastonite = CaSiO₃

potential of the relatively small amount of fly ash produced from coal combustion would be about two orders of magnitude smaller than the CO₂ produced from that combustion.

5. Novel process concepts

5.1 Autoclaving

As noted above, Fagerlund and Zevenhoven, (2011) and Nduagu et al. (2012) have focussed their research on the use of hydroxides derived from silicate minerals. They have determined that useful rates of reaction require conditions of high temperature and high pressure, such as 400-500°C and 25 bar.

The requirement for conditions of high temperature and pressure in the traditional industrial context presents a barrier to practical implementation when the energy consumption consequences are considered.

5.2 The GPV reactor

A novel approach for greatly reducing, and theoretically eliminating, that large energy penalty has been modelled by Santos et al (2013) using the concept of the patented Gravity Pressure Vessel (GPV). The GPV consists of three concentric metal tubes set in a deep hole drilled and cased in the manner of an oil well. The reactants would be fed down a central tube where increasing hydrostatic pressure would provide the pressurisation. An exothermic reaction would provide a high temperature zone at the bottom of the GPV reactor. The hot reactants returning up the annulus would preheat the feed. It is proposed that an outer annulus would be evacuated to minimise heat loss into the surrounding formations. Santos et al (2013) describe the GPV as “*This is a special kind of autoclave with a built in heat exchanger, plug flow configuration and gravity driven pressurisation. Residence time is controlled by the reactor length that can reach up to 2400m, resulting in hydrostatic built pressure that can reach 120 bar.*” The GPV concept is being developed by others with a view to processing of aqueous biomass mixtures to yield valuable chemicals and hydrocarbons. The prospect of carrying out a mineral processing reaction of a three-phase slurry at the bottom of a 2.4 km deep pipe with an abrupt change of flow direction suggests that solid deposition and blockage of the GPV reactor in that inaccessible location might be an insurmountable problem.

5.3 Catalysis

The use of oxalates or citrates to catalyse the olivine dissolution reaction have been explored by Prigiobbe and Mazzotti (2011) under conditions of elevated temperature and high CO₂ partial pressure. They found a catalytic effect of up to an order of magnitude on the reaction rate but that effect was dependent on acidity, requiring conditions in the range of 2-5 pH. Again, this more extreme processing environment suggests that adequate acceleration of the

carbonation reaction does not suggest a technically and economically feasible large scale means of CO₂ sequestration.

6. Environmental and Health Issues

Although carbonation may potentially store CO₂ indefinitely over geological time, the environmental side effects of the process involved need to be considered.

Mining on the scale required would disturb huge amounts of land and natural habitats and has the potential to cause large scale ecological damage. The environmental impact of this would need assessing before any mining could take place. A mineral mine located near a settlement could also cause light and noise pollution for residents and increased traffic.

As discussed, mined silicates for ex-situ use are ground down to a fine dust before use. The effects and toxicity of finely ground olivine is currently unknown, although fine particulate matter is often believed to be a leading cause of respiratory disease (Koornneef J & Nieuwlaar, IP). It is noted that asbestos is a form of the serpentine mineral.

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