



GHGT-10

Review of the various CO₂ mineralization product forms

Marcel Verduyn^{a,1*}, Hans Geerlings^{a,b}, Gert van Mossel^a,

Sivakumar Vijayakumari^a

^aShell Global Solutions International B.V.,
Grasweg 31, 1031 HW Amsterdam, THE NETHERLANDS

^bDelft University of Technology, Faculty of Applied Sciences – Department of Chemical Engineering,
Julianalaan 136, 2628 BL Delft, THE NETHERLANDS

Abstract

Two experimental modes of operation, a sequence of batch and a continuous one, have demonstrated the technical feasibility of Shell's proposed slurry-based direct flue gas mineralization concept on the basis of activated serpentine. The base case mineralization concept can be simplified yielding a variety of product forms and significantly reduced CO₂ abatement costs. Combined with a positive first assessment of the sustainability of the various mineralization product forms, all mineralization concepts deserve to be further investigated. To optimally take advantage of integration opportunities so as avoid parasitic CO₂ emissions and minimize cost, this should be done over the complete technology chain.

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* Corresponding author. Tel.: +31-20-630-2649; fax: +31-20-630-3964
E-mail address: marcel.verduyn@shell.com

1. Introduction

Carbon capture and sequestration (CCS) is an important option for CO₂ mitigation. Carbon dioxide carbonation, *i.e.* mineralization, is one of the CCS options; others include geological storage in aquifers and (empty) oil and gas fields. The need for such a portfolio of CO₂ emission reduction technologies to reach sufficient global reduction of CO₂ emissions can nicely be shown by wedges following the publication of Pacala and Socolow in Science [1]:

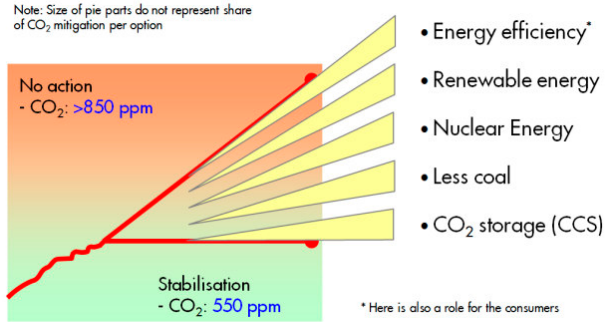


Figure 1. Stabilization wedges illustrating the need for application of a portfolio of CO₂ mitigation technologies

CCS solutions at all scales will be required to meet the worldwide targets for CO₂ reduction. Mineralization CCS is a scalable approach to CCS where CO₂ is reacted with suitable calcium or magnesium containing minerals to capture and store carbon emissions in a solid form. It is recognized by the IPCC as an important part of the CCS technology portfolio since the resulting storage “is highly verifiable and unquestionably permanent” [2]. It is an accelerated natural weathering process.

A further dimension driving interest in mineralization CCS is that the IEA has shown [3] that 26% of the CO₂ mitigation from CCS will come from the fuel transformation sector and 20% from industry, such as cement and steel production. It is unlikely that the scaling down of dense phase CCS systems from large, central power generation or refinery facilities to distributed energy systems or industrial processes will result in an economically viable option.

So-called ‘abatement curves’ are often used. In there, the prognosed costs (expressed in \$/t CO₂ avoided) of different mitigation technologies are plotted as a function of the expected deployment (Gt/a CO₂ avoided).

2. Mineralization feedstock

During any mineralization process, cations (Mg²⁺, Ca²⁺) from the feedstock react with CO₂ to form carbonates, either CO₃²⁻ or HCO₃⁻.

Different feedstocks can be employed, magnesium silicates such as olivine and serpentine, wollastonite, a calcium silicate as well as industrial waste materials such as steel slag, fly ash etc. Because they provide the most abundant resource base, the ultimate Shell focus has been on ultramafic rocks, in particular serpentine, Mg₃Si₂O₅(OH)₄, a phyllosilicate (*i.e.* with a sheet crystal structure).

The feedstocks differ in reactivity. Our experimental findings show that thermally activated serpentine can be used for direct flue gas mineralization using Shell's process concept, whilst olivine to a much lesser extent because it requires elevated temperatures during mineralization. The most plausible reason is the crystallinity of olivine. During thermal activation of serpentine, which partial dehydroxylates its crystal water, a reactive amorphous phase having a chemical composition similar, but not equal to, olivine is being formed [4].

Shell's direct flue gas mineralization technology is slurry-based. Following the carbonate precipitation step, removal of the aqueous phase is optional. It is possible to use demineralized water but also seawater.

3. Illustration of mineralization process concepts

Initially, the leaching of cations and their subsequent precipitation were carried out in a single step [5]. For precipitation to occur, the solubility products of the carbonates have to be exceeded. This is done by operating at an elevated temperature, typically in the range 110 to 140 °C. However, to counteract the resulting decrease of CO₂ solubility, CO₂ streams having a high CO₂ partial pressure (mostly pure CO₂, which needs to be separated from the flue gas in advance) are fed to the reactor. A sketch of the process is given below.

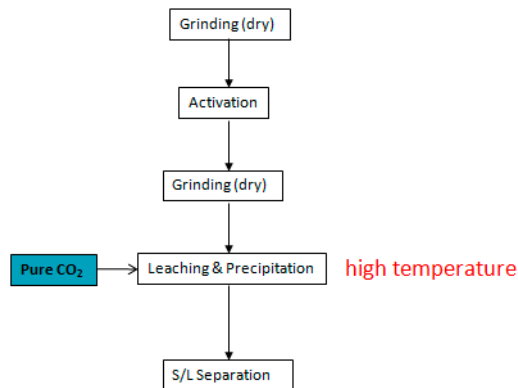


Figure 2. Initial mineralization process concept for pure CO₂

Flue gas having a slightly above atmospheric pressure with a CO₂ concentration of about 10 %vol (note, this is about the average of coal and gas fired power plant) of course has a much lower solubility than pure CO₂ at pressure. For this reason the pH is higher and the required leaching of cations will take place at a much slower rate.

To be able to counteract this, contacting of the flue gas with the mineral slurry is separately done at ambient temperatures in a slurry mill and in a leaching basin. This process concept, sketched in Fig. 3, yields a dry mineralization product consisting of magnesite, silica, and some unconverted material. Of course the individual process steps are operated at optimal conditions.

Worthwhile mentioning in this context is that our internal focus has been the exploration of the core CO₂ mineralization technology (enabling the mineralization reaction itself), well realizing that in practice both upstream (e.g. mining, transport logistics) and downstream (e.g. product use or disposal) unit operations must also be taken into account.

Process integration and simplification over the complete technology chain is an absolute *must* in developing a viable mineralization process because it reduces operating costs and minimizes parasitic CO₂ emissions.

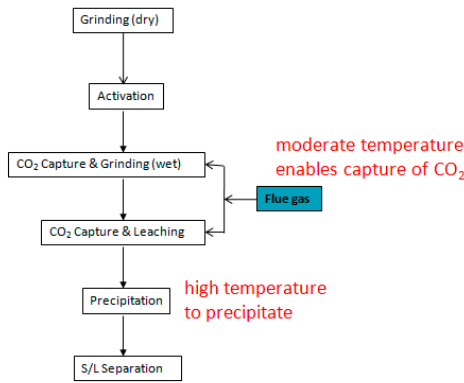


Figure 3. Direct flue gas mineralization process concept

4. Mineralization product forms

A simplification of the direct flue gas mineralization process concept described above, called base case, reduces process costs. These process simplifications yield different mineralization product forms. We will show that all process configurations yield a usable and sustainable mineralization product output stream.

The figure below shows the base case and two process simplifications. The upper part is considered the essential backbone of the direct flue gas mineralization process.

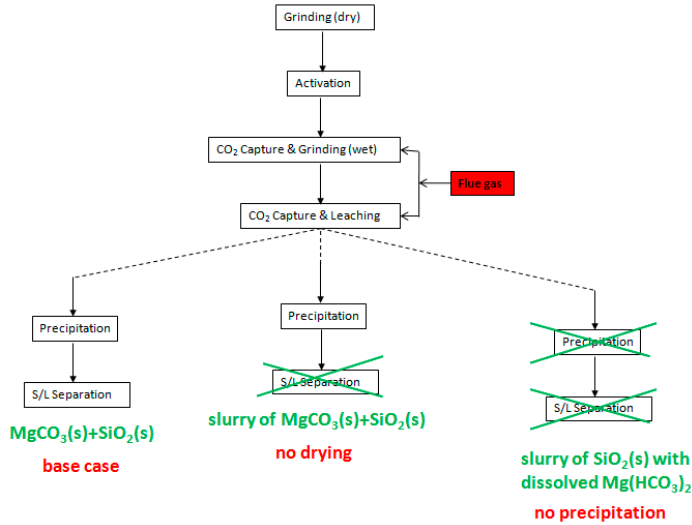


Figure 4. Process simplifications and the resulting alternative mineralization product forms

Besides the stoichiometric advantage of yielding dissolved magnesium bicarbonate, not using a magnesium carbonate precipitation unit has a large cost advantage. Moreover, omitting any thermal unit operation for drying the mineralization product slurry leads to a large cost reduction. This is shown in the following staircase graph. It is important to emphasize that neither costs, nor benefits on the upstream (e.g. mineral mining) and downstream (e.g. product valorization) side of the core mineral carbonation process have been taken into account when making these cost estimates.

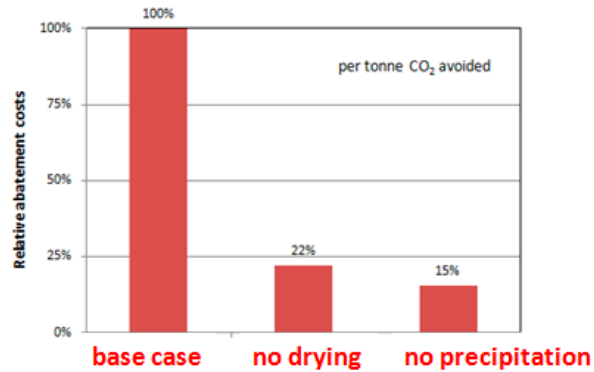


Figure 5. Staircase graph of cost reduction by change of mineralization product form (incremental changes)

As mentioned before, research and development of CO₂ mineralization has focused to a dominant extent on the core mineralization process. Nevertheless, it is well possible to address the downstream side and indicate potential applications or application areas of the mineralization products. During all mineralization routes described in Fig. 4, a solid is formed. It consists of μm sized particles having a tendency to aggregate.

A key mineralization product application, for both solid and slurry form, would be land expansion. The spreading of a sand slurry, as Fig. 6 shows, is common practice.



Figure 6. Spreading of sand slurry for land expansion purposes

The mineralization products could be used for a variety of further application areas such as filler in construction materials such as concrete or in bitumen to build roads.

It is worth noting that CO₂ mineralization is the only technology option that can simultaneously mitigate CO₂ and remediate the effects of global warming by using the mineralization product forms for instance for building dikes, creating water buffers or for land reclamation. In certain areas this could be a key differentiator in the portfolio of CO₂ mitigation options.

We have made a first assessment of the sustainability of the different mineralization product forms. The key points are summarized below. Following this assessment we conclude that all mineralization product forms seem sustainable.

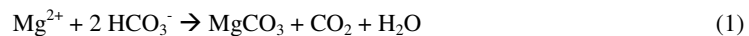
MgCO₃

As Allen and Brent [6] recently reported, when MgCO₃ is exposed to typical rain/weather conditions, there is negligible CO₂ leakage. In fact, even when some of the MgCO₃ dissolves, there no net release of CO₂ because dissolved Mg(HCO₃)₂ is formed.

Dissolved Mg(HCO₃)₂

In this product form, two bicarbonate ions are accompanied by one magnesium cation, a clear stoichiometric advantage as compared to solid magnesium carbonate.

The endothermic precipitation of MgCO₃ from dissolved magnesium bicarbonate takes place via the following reaction equation



during which CO₂ is released.

In nature, the weathering of magnesium silicates also yields dissolved Mg(HCO₃)₂. Still, MgCO₃ deposits are rare even when formed over geological time scales. The reason is that due to kinetic effects (low concentrations) the solubility product is only remote, and hence, despite thermodynamically favoured, the precipitation of MgCO₃ does not take place. In marine systems, a rapid mixing can be provided, hence keeping concentration changes very small.

It is important to mention that CaCO₃ has a much lower solubility than MgCO₃. Still, calcium bicarbonate is oversaturated in marine environments. The reason is that its precipitation takes place through biological pathways.

5. Technical feasibility of the direct flue gas mineralization concept

The technical feasibility of the concept was investigated experimentally using a serpentine feedstock (i.e. rich in serpentine). Because for most of the individual process steps a kind of ‘learning curve’ in terms of efficiency and operability had to be followed, it was decided to first represent the direct flue gas mineralization concept by a sequence of batch steps.

The learnings thereof were translated into the design of a continuous unit. The unit has been commissioned, taken into operation and the initial results that are being obtained confirm the technical feasibility of Shell’s direct flue gas mineralization concept.

The next two subsections provide further details about the two modes of experimental investigation.

5.1 Sequence of batch steps

Based on the concept drawn in Fig. 3, the laboratory equipment used to obtain proof of principle is seen in the following photographs:

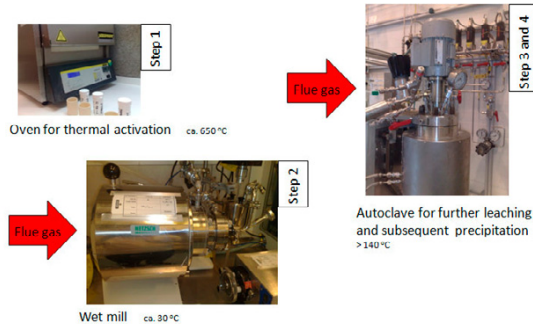


Figure 7. Illustration of batch laboratory equipment used to obtain proof of principle

Within the slurry mill a simultaneous contacting with the gas phase takes place.

5.2 Continuous operation

The Energy Centre of the Netherlands (ECN) in Petten was contracted to translate our insights and batch experimental findings into a continuous process. Building further on the results from the sequence of batch steps, continuous results form further demonstration of the technical feasibility of this flue gas mineralization concept.



Figure 8. Illustration of continuous direct flue gas mineralization unit

This versatile unit, built in a modular way, allows to investigate a variety of process concepts, conditions and cation carriers (serpentine, olivine, steel slag, ...). Again, the slurry mill with simultaneous flue gas contacting forms an essential element within this process concept.

Few further characteristics of the continuous unit:

- Mineral throughput max. 1 kg/h
- Broad operability (max. temperature 200 °C (with pH sensor 130 °C), max. pressure 45 bara)

- Chloride resistant materials
- Skid mounted, container size
- Automated operation

6. Results and discussion

Both experimental modes of operation, sequence of batch and continuous, have demonstrated the technical feasibility of Shell's proposed direct flue gas mineralization concept on the basis of activated serpentine. Typically, serpentine mineral rocks also contain olivine. It is important to mention that in the autoclave, olivine will be converted as well.

The slurry mill with simultaneous gas contacting fulfills an essential role within Shell's direct flue gas mineralization process. It achieves both a huge reduction of particle size and the formation of carbonate intermediates other than bicarbonate, for instance hydromagnesite.

The continuous experiments show that seawater can also be employed as aqueous phase. The use of seawater accelerates rate of leaching and subsequent precipitation. Nevertheless, seawater requires particular attention regarding material choice for instance for level control sensors onto which deposits are formed.

It is possible to simplify the base case mineralization concept yielding a variety of product forms and significantly reduced abatement costs. Combined with the positive first assessment of the sustainability of the various mineralization product forms, all mineralization concepts deserve to be pursued further.

7. Conclusions

Two experimental modes of operation, a sequence of batch and a continuous one, have demonstrated the technical feasibility of Shell's proposed slurry-based direct flue gas mineralization concept. Activated serpentine mineral rock is a suitable feedstock for the direct flue gas mineralization concept.

The base case mineralization concept can be simplified yielding a variety of product forms and significantly reduced CO₂ abatement costs. Combined with a positive first assessment of the sustainability of the various mineralization product forms, all mineralization concepts deserve to be further investigated.

To push CO₂ mineralization further through the technology development funnel and reduce CO₂ abatement costs as well as minimize parasitic CO₂ emissions, continued optimization, simplification and process integration over the complete technology chain are required. Research and development will continue to have an important place therein.

8. References

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