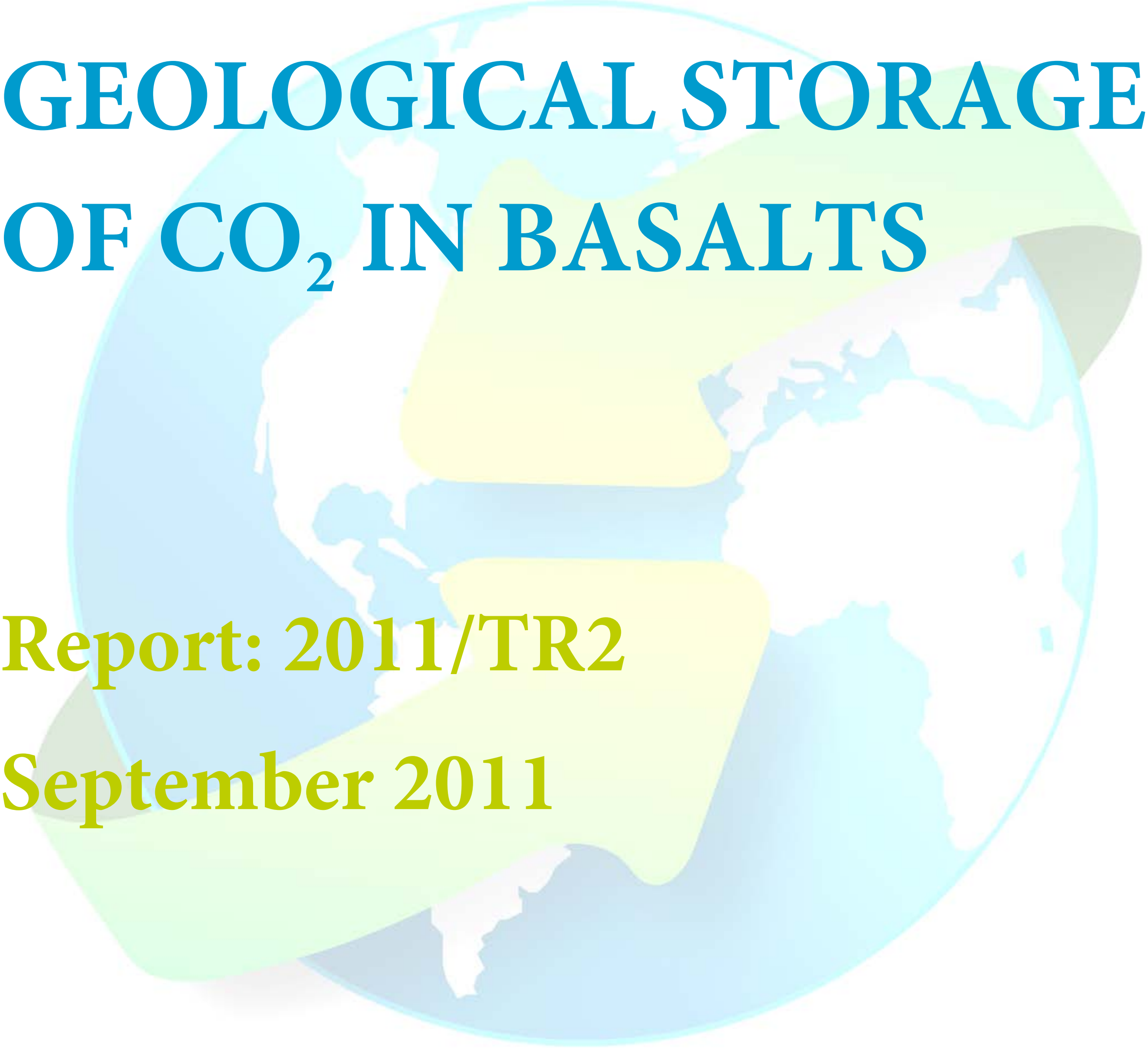
GEOLOGICAL STORAGE OF CO_2 IN BASALTS



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Executive Summary

This technical review has been undertaken with the aim of providing a high level overview of the current status of basalts as an option for geological storage of CO_2

Basalts are formed by the solidification of lava from volcanic eruptions, often in a series of repeated events that lead to the accumulation of thick sequences. Large basaltic deposits occur in several regions around the world and both onshore and offshore deposits have been considered as storage options. Such deposits often exist in areas where there are no other storage opportunities and so may be worth exploring. The volumes of most deposits are known, however, the storage capacity is still to be assessed in most areas and where it has been assessed there is a very high level of uncertainty, as capacity and injectivity will depend on permeability, which depends on the interconnectedness of the fracture network. One area that has been assessed for capacity is the Columbia River Basalt Group; with estimated storage capacity of 10 to 50 Gt of CO_2 (McGrail et al, 2010).

Basalts are composed of of minerals with high proportions of Mg, Fe and Ca, which can react with CO_2 to form stable carbonate minerals. This offers potential storage security and is one of the major benefits of storing CO_2 in basalts. There is uncertainty in which reactions will take place and their timescales, especially in regards to reactions involving supercritical CO_2. In-situ mineralisation of CO_2 in basalts is feasible as has been shown in laboratory experiments and modelling studies, but yet to be tested as injection has not yet started at either of the two current pilot sites.

To allow injection, it is necessary to have relatively high porosity and permeability within the storage reservoir. This is likely to be found in the upper layer of each basalt layer or flow; which may be fractured and brecciated, due to vesiculation (vesicles are cavities within the basalt, formed by air bubbles rising to the top of the lava flows), secondary fracturing (e.g. cooling during solidification of the basaltic lava) and weathering from exposure. The interconnectedness of the fracture network and vesicles also needs to be considered as this will change the effective porosity. As volcanic eruptions are cyclic events, there are expected to be several layers of flows. Therefore rocks with similar compositions to basalt but without porous and permeable layers would not act well as a storage reservoir. The grain size is also of significance as coarser grained rocks; such as dolerites and gabbros will have smaller mineral surface areas compared to finer grained basalt, which will effect reactions with fluids in the fractures. Therefore, rocks with similar compositions to basalt, but with coarser grain sizes such as dolerites are unlikely to act well as a storage reservoir, due to the lack of any permeable layers.

Containment of CO_2 will be affected by fractures and fracture interconnectivity within the ‘caprock’ layers. These could already exist within the formation or come about by secondary fracturing of the overburden during injection. Risk of leakage via fractures will need to be considered, especially as basalts have a low ductility. It is also possible that any CO_2 migrating through fractures will be mineralised before reaching the surface, which could retard any migration, however this depends on the rate of mineralisation. This is still an uncertainty.

The two planned pilot projects are one in the pacific northwest of the US into the Columbia River basalt group, the Wallula pilot project; and one into a basaltic reservoir in Iceland; the CarbFix project. These projects are very different in nature, with the CarbFix project intending to inject pre-dissolved CO_2 into a 400m deep basaltic formation, thereby eliminating the risk of leakage and the Wallula project intending to inject supercritical CO_2 at a depth of 900m into an interflow zone of 3 separate flows. The interflow zone is highly fractured; and the porosity and permeability is expected to much higher that the main body of the flow; which is formed of a more crystalline structure of very low permeability.

Though injection has not yet started at either injection site, there has been much progress through site characterisations and laboratory and modelling studies and therefore, increased understanding of the CO_2-rock reactions expected to take place. However, while reactions of aqueous CO_2 are considered to be very well understood, knowledge of supercritical CO_2 – rock reactions, while improved greatly, are still considered a knowledge gap. This is in regards to the type of minerals expected to be produced and the reaction rates to be expected. Further research in all these areas is ongoing.

The majority of work has been carried out regarding onshore basalt storage of CO_2, but some studies have considered the feasibility of storage offshore, which has the added benefits of blanketing deep-sea sediments forming a low-permeability stratigraphic barrier, in the case of leakage at such a depth hydrates are likely to form thereby trapping the leaked CO_2 and at water depths greater than 2700m there will be gravitational trapping as the CO_2 will be more dense than seawater.

It is highly uncertain when basalt storage could be possible on a commercial scale; even assuming the pilot projects described above are successful. If compared to storage in deep saline formations (DSF), for which research started almost 30 years ago, then it may similarly be decades before basalt storage reaches the same level. However some learning from DSF may be applicable to basalt storage, shortening the time for commercialisation.

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GEOLOGICAL STORAGE OF CO_2 IN BASALTS

1. Introduction

The largest potential for geological storage of CO_2 is considered to be within deep saline formations (DSF) and though these formations occur on a wide scale, they do not exist in all regions and other storage options may need to be considered. In several regions around the world there are large basaltic deposits both onshore and offshore, some of which are being considered as storage options. A major benefit of storage within basaltic formations would be that some chemical components within basalt react with CO_2 to form stable minerals, thereby greatly increasing the storage security. There is uncertainty in which reactions will take place and their timescales and there is ongoing research in this area.

2. Storage Mechanisms

Basalt formations usually exist as layered flows, representing a series of volcanic eruptions over time. During an eruption molten rock flows from the volcano; the lower part takes a longer time to cool and forms a crystalline structure. The lighter air bubbles flow to the top of the lava, forming vesicles (small cavities formed in volcanic rock by entrapment of gas bubbles during solidification). As this is the top of the flow, it cools more quickly, forming smaller crystals. Following an eruption is a period of little or no volcanic activity, during which time the flow tops are eroded and weathered and plants are likely to grow forming fractures within the rock. Volcanic eruptions are generally cyclic events and so a typical basaltic sequence will contain several flows overlying each other.

Basalt in the tops of subaerial lava flows will often be highly vesiculated (containing vesicles), imparting a lightweight "frothy" texture to the rock. While the underlying lava, having had more time to cool down and solidify will form a more crystalline texture. The flow tops containing vesicles and fractures can have a relatively high permeability compared to the impermeable main flow, though it is necessary for the vesicles to be interconnected by fractures to make use of their porosity. The brecciated flow top layers would therefore be able to act as the storage formation and the main flow body as the caprock. As there will be several flows overlying each other; there may be several reservoir-caprock layers.

Some key factors affecting the capacity and injectivity of CO_2 into basalt formations are effective porosity of flow top layers and interconnectivity (DoE, 2010)

For a high injectivity, it is necessary to have a high connectivity within the fracture network in the reservoir layer and this is still considered an uncertainty. Vesicles in the flow top layer increase the porosity, but unless these are interconnected through the fracture network, the effective porosity will be lower.

Like all storage sites, containment of CO_2 needs to be considered. This is affected by the presence of fractures as well as their interconnectivity within the ‘caprock’ layers. These could already exist within the formation or come about by secondary fracturing of the overburden during injection.

Injection simulation for the Wallula pilot project (McGrail et al, 2010) suggests sufficient permeability in the storage reservoir to allow injection and avoid excessive pressures. There is still uncertainty in this area as injection is yet to start.

Risk of leakage via fractures is something that will need to be considered, especially as basalts have a low ductility. It is also possible that any CO_2 migrating through secondary fractures will be mineralised before reaching the surface. However, there is uncertainty related to this.

In addition to structural trapping, the main advantage of basalt as a storage formation is the chemical reactions that allow mineral trapping of CO_2 by formation of carbonates. Such reactions often occur naturally as secondary mineral formation when CO_2 rich saline water enters the formation.

Significant quantities of Ca, Mg and Fe in basaltic formations are the basis for chemical reactions that allow mineral trapping. Groundwater within a basaltic formation will typically be brackish with a pH from 8.5 to 9.2. Injection of CO_2 reduces the pH to 3.5 or lower (McGrail et al, 2003). Iron rich phases within the formation, such as pyroxene, olivine and spinel are unstable at a low pH and dissolution occurs. The iron then reacts with CO_2 to form ferrous carbonate minerals, such as siderite.

Experiments on the rate and type of reactions have been carried out at the Pacific Northwest National Laboratories and are described in Schaef et al (2010). Well cuttings of Columbia River basalt and Central Atlantic Magmatic Province basalt show the different reactions from aqueous dissolved CO_2 and supercritical CO_2. The experiments were carried out over a range of temperatures and pressures to illustrate the effects of depth on basalt reactivity and carbonation.

The results of the experiment show that with increased simulated depth there were more carbonate precipitates. This is evidence that the basalts are less stable with increasing depth, dissolving quicker to release cation-forming carbonates. At shallower depths calcite is formed, showing that Ca^{2+} is dominant; as depth increases the concentration of other cations increases, such as Fe^{2+}, Mg^{2+} and Mn^{2+}, which could be an indication of certain components, such as pyroxenes becoming less stable.

Reactions with water rich supercritical CO_2 ($scCO_2$) are not as well understood as those with the aqueous solution, but the experiments show distinctly different products. The wet CO_2 experiments form smaller, but more abundant minerals, sometimes completely coating the basalt surface. Further work is being carried out in this area to understand the dynamics involved in these reactions.

Gislason et al (2010) describe the most significant reactions expected if CO_2 is dissolved in water. These are:

1. $CO_{2(g)} + H_2O = H_2CO_3$
2. $H_2CO_3 = HCO_3^- + H^+$
3. $(Fe, Ca, Mg)^{2+} + CO_2 + H_2O = (Fe, Ca, Mg)CO_3 + H^+$

4. $Mg_2SiO_4 + 4H^+ \rightarrow 2Mg^{2+} + 2H_2O + SiO_{2(aq)}$
5. $CaAl_2Si_2O_8 + 8H^+ \rightarrow Ca^{2+} + 2Al^{3+} + 2SiO_{2(aq)} + 4H_2O$

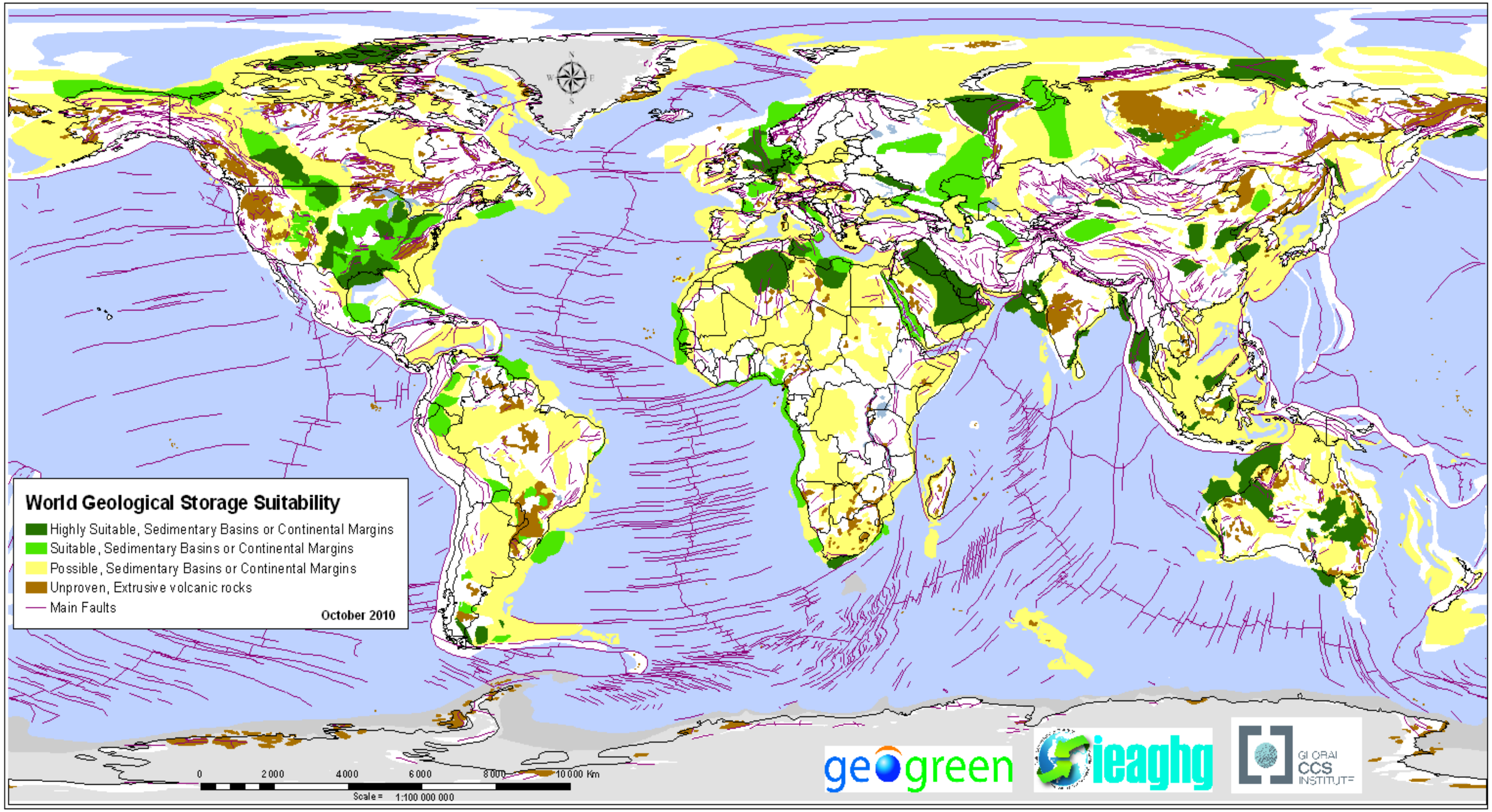
Equations 1 and 2 simply describe CO_2 dissolution in water, equation 3 describes metal cations expected in the formation water in basalts forming carbonates. All of these reactions produce H^+ ions, which need to be consumed for further carbonation to take place. This occurs in reactions 4 and 5 (amongst others) by reaction with silicates, forming the cations needed to form carbonates.

It is important to note that even though the main trapping mechanism is expected to be mineralisation; a certain porosity and permeability, though vesiculation and fracturing is necessary to enable injection into the basalt in the first place. Therefore rocks with similar compositions to basalt but without porous and permeable layers would not act well as a storage reservoir. The grain size is also of significance as coarser grained rocks, such as dolerites and gabbros will have smaller mineral surface areas compared to finer grained basalt, which will effect reactions with fluids in the fractures.

3. Potential Storage Locations

Basalt deposits can be found across the world, though there has been very little characterisation of these deposits for the purpose of geological storage of CO_2. Figure 1 (IEAGHG/ GCCSI, 2011) shows the location of potential storage locations, with the basalt (in brown) represented as unproven storage.

Fig. 1: Storage Suitability map (Basalts are the brown areas)



For many areas, e.g. India, this could prove to be a significant resource if found to be appropriate for geological storage of CO_2. The following table taken from McGrail et al (2003) gives more information on the volume of basalt in major basaltic provinces, though other small basalt accumulations may also be considered for storage. The most significant in the table are those in the U.S, China and India due to the current and future amount of CO_2 expected to be emitted.

Table 1 Major Basaltic Provinces

Large Igneous Province	**Location**	**Area, km^2**	**Volume, km^3**
Columbia River Basalt Group	Northwestern U.S.	200,000	224,000
Deccan Traps	India and Pakistan	600,00	512,000
Emeishan basalts	Southwest China	>250,000	>300,000
Hannuoba-Chifeng basalts	Northeast China	20,000	1400*
Kerguelen Plateau	Southern Indian Ocean	2,300,000	9,100,000
Keweenawan Basalts	Northcentral U.S.	160,000	640,000*
North Atlantic Volcanic Province	UK and Greenland	1,300,000	6,600,000
Newark Basin and Hartford Basin	Northeastern U.S.	500*/400*	50*/40*
Ontong Java Plateau	Southwestern Pacific	1,900,000	44,400,000
Parana-Etendeka Province	Brazil, Namibia and Angola	2,200,000	>1,000,000
Siberian Traps	Eastern Siberia	340,000	400,000
Yemen-Ethiopian Traps	Yemen and Ethiopia	>600,000	>350,000

* Estimated. Volumes estimated from area and average thickness 70m (HCB), 4km (KEW) and 100m (NB/HB)

Schaef et al (2010) give results of experiments carried out on basaltic rocks from different locations around the world, which show the differences in the expected mineral reactions on injecting CO_2. The basalts used for the comparison were the Columbia River Basalt Group, Central Atlantic Magmatic Province and Newark Basins in the US, the Deccan Traps in India and the Karoo basin in South Africa. It should be noted that these experiments do not take into account larger scale structures; i.e. whether or not there are suitable interflow zones as described in section 2.

The results show that when using a pure $scCO_2$-water system, the Newark Basin basalts were the most reactive and the Karoo basin the least, though no convincing correlations were found relating the reactivity to bulk composition or mineralogy. Addition of H_2S to the system enhanced carbonation in the Karoo and Columbia River basalts, but inhibited carbonation in the Newark Basin basalts due to precipitation of pyrite that formed a protective layer around the grains.

Carbon dioxide storage in deep-sea basalt has been suggested by Goldberg et al (2008) with the added benefits of blanketing deep-sea sediments forming a low-permeability stratigraphic barrier, in the case of leakage at such a depth hydrates are likely to form thereby trapping the leaked CO_2 and at water depths greater than 2700m there will be gravitational trapping as the CO_2 will be more dense than seawater.

Goldberg and Slagle (2009) then go on to estimate the global capacity of deep-sea basalts, which gives a total theoretical total worldwide storage capacity of 2000 – 11,000 Gt.CO_2. It should be emphasised that there has yet to be any research in deep-sea basalt storage, beyond the theoretical.

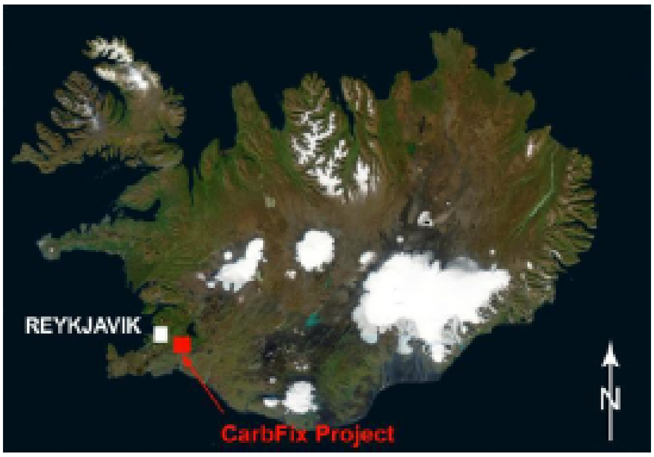
4. Real Projects

There has yet to be any injection into basalt, but there are pilot projects where injection is expected to commence in the near future.

4.1 Carbfix Project, Iceland

The Carbfix project is located at Hellisheidi (Figure 2) in Iceland and was initiated in 2007 and consists of a field-scale CO_2 injection into basalt, laboratory experiments on dissolution and precipitation and dissolution kinetics, geochemical modelling and the study of natural CO_2-rich waters as a natural analogue.

Figure 2: Location of the Carbfix Project (from Matter et al, 2009)



The project is described by Matter et al (2009) and updated to include further proposed monitoring techniques by Matter et al (2010).

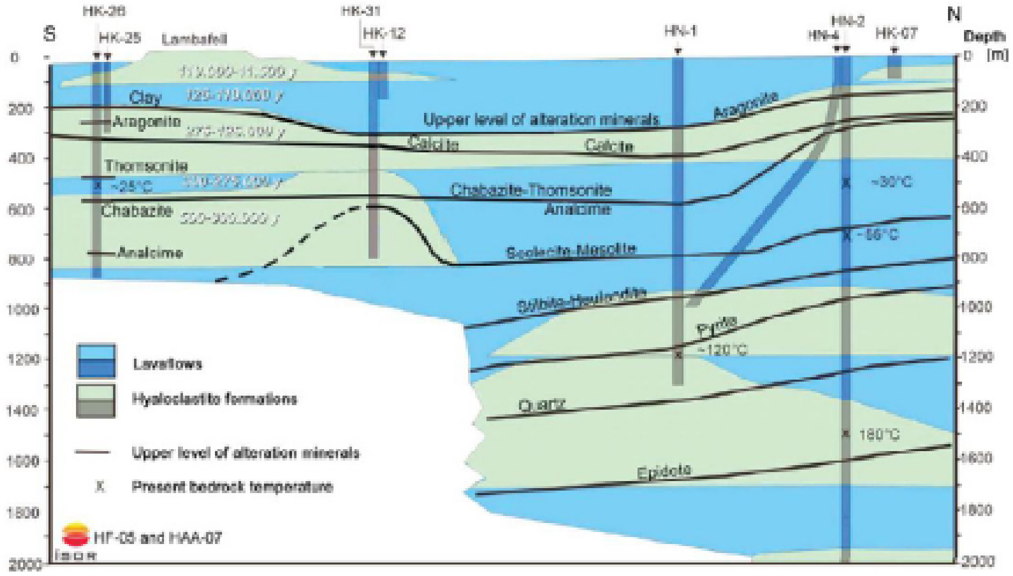
The geothermal power plant in Hellisheidi produces 60 kt of CO_2 per year; 2200t/yr from this will be captured and reinjected into the target formation, which is located at a depth of 400 – 800m depth. At this depth the carbon dioxide is naturally in a gaseous state and to enhance in-situ mineralisation, the CO_2 will be dissolved in water from the geothermal reservoir prior to injection. In-situ mineralisation is likely to be optimised as the required chemical components needed for the mineralisation reactions will be in the correct proportions.

Gislason et al (2009) describe in detail the thermodynamic and kinetic basis for mineral storage in basalt and how it can be optimised. When the CO_2 is dissolved in water, CO_2^{2-} are formed, which will then be able to react with Ca, Mg and Fe cations that are expected to be present in basaltic rocks. Both of these reactions produce H^+ ions, which need to be consumed for these reactions to take place. This can happen by reaction with Mg, Ca and Al silicates.

The amount of water required for dissolution of CO_2 is dependent on pressure temperature and salinity. The CO_2 and water mix will be injected at a partial pressure of 25 bars and 25°C and at these conditions 1 t CO_2 requires approximately 27 t water.

A geological cross-section of the injection zone can be seen in figure 3, where the injection will be into HK-2.

Figure 3: Injection scenario (from Matter et al, 2010)



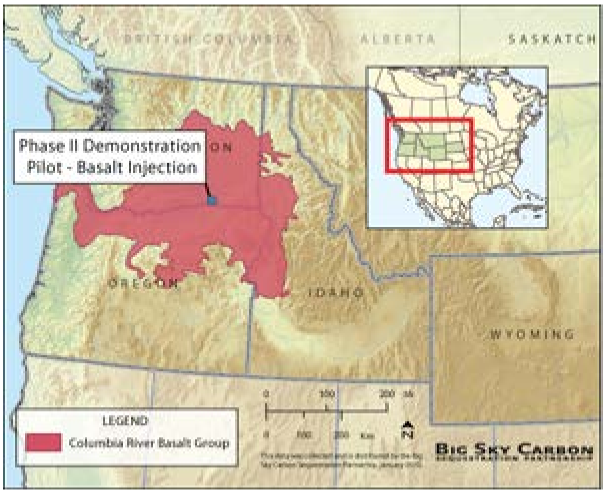
As the CO_2 is dissolved in water, standard geophysical techniques, such as seismic surveys will not be able to easily differentiate between the injected CO_2 and the in-situ fluids, so a geochemical tracer approach is to be taken. Tracers; SF_5CF_3 and acid red dye (Amidorhodamine G) will be mixed into the gas water stream to monitor and characterise the transport processes of CO_2. The injected CO_2 will also be tagged with radiocarbon (^{14}C). This is used because the reservoir is expected to be generally free on ^{14}C and because it is a reactive tracer, therefore can be used to monitor the amount of carbonation that has taken place. Using this multi tracer approach will allow monitoring of physical and chemical processes separately.

When using commercial downhole samplers, gas bubbles are commonly observed, which is unsuitable for monitoring CO_2 charged waters. A piston-type downhole sampler has been designed (Alfredsson et al 2010) to avoid gas bubbles and increase the quality of downhole monitoring.

4.2 Wallula Basalt Project, Pacific Northwest

The Wallula pilot project is situated in deep basalts of the Miocene Columbia River Basalt Group (CRBG), which cover an area of 200,000 km^2 over Washington, Oregon and Idaho (figure 4). Over 300 individual CRBG flows have been identified in the region with a maximum composite thickness of 5km within the central portion. An estimate of storage capacity of the entire CRBG is given in McGrail et al (2010) of 10 to 50Gt of CO_2.

Figure 4: Location of the Wallula Basalt Project



(from http://bigskyco2.org/research/geologic/basalt_project)

Site selection and characterisation has been carried out extensively (McGrail et al 2010) in the form of soil gas monitoring wells, seismic surveys, borehole drilling and characterisation, stratigraphic and geochemical sampling, wireline logs and hydrologic testing.

Soil gas monitoring wells show elevated readings for N_2 and O_2; CO_2 concentrations were identical or lower than background levels and methane levels were below detectable limits. Elevated methane levels can be indicative of flow conduits bringing methane from deeper levels and the absence of this may suggest the absence of high flux conduits, such as faults and fractures.

Traditional seismic methods have not been successful in imaging basalt features in on-shore areas where the basalt is overlain by a thin cover of sediment due to a wide variety of shear wave modes. By removing s-wave components and other noise there is a vast improvement in image quality (Sullivan et al, 2010). The results from these experiments may be useful for any other areas where onshore basalt storage is being considered. The processed seismic surveys showed a thick succession of basalt layers undisturbed by faulting.

The ‘drill-and-test’ characterisation strategy was used, which increased the quality of data specifically for hydrological parameters sensitive to the drilling process, such as hydrochemistry and microbiology. Following the casing of the well, wireline logging was carried out, which showed porosity to be 15 to 30% in the brecciated flow tops and from 15 to 25% in the proposed injection zones. The logging data also indicate no major faults in the well. The hydrological tests show the formation water not to be of drinking water standard, due to the pH, fluoride and iron content and the flow tops to have a moderate permeability of 75 to 150 mD, bounded by thick flow interiors with microdarcy scale permeability.

The intended injection zone is an interflow zone of 3 separate flows at 900m depth.

Injection simulation analysis modelled 1000 t of supercritical CO_2 injected over 14 or 30 days, which show acceptable pressure increases and after 1 year of injection, 18% of the injected CO_2 to have dissolved into the aqueous groundwater phase. The entire 1000 t of CO_2 is expected to have completely mineralised in 10 years (McGrail, 2010 in answer to a question at GHGT-10).

The permitting process to inject CO_2 is underway and injection expected to commence in 2011.

5. Conclusions

In-situ mineralisation of CO_2 in basalts is potentially feasible and has been demonstrated in laboratory experiments and modelling studies, but has yet to be tested at the pilot scale. Adequate storage capacity and injectivity is possible due to the porosity and permeability caused by fracturing in the top layers of each basalt flow. However, as there is currently no real life injection data; there is still high uncertainty related to injectivity.

The Wallula and CarbFix pilot projects have carried out extensive site investigation and experimentation and modelling. These projects are very different in nature, with the CarbFix project intending to inject pre-dissolved CO_2 into a 400m deep aquifer and the Wallula project intending to inject supercritical CO_2 at a depth of 900m.

Though injection has not yet started at either injection site, there has been much progress through site characterisations and laboratory and modelling studies and therefore, increased understanding of the CO_2-rock reactions expected to take place. However, while reactions of aqueous CO_2 are considered to be very well understood, knowledge of supercritical CO_2 – rock reactions, while improved greatly, is still considered a knowledge gap. This is in regards to the type of minerals expected to be produced and the reaction rates to be expected. Further research in all these areas is ongoing.

Injection dates at both sites have been repeatedly pushed back, but injection is expected to commence sometime this year.

The majority of work has been carried out regarding onshore basalt storage of CO_2, but some studies have considered the feasibility of storage offshore, though these studies are still theoretical at this stage.

It is uncertain how long it will be before basalt storage will be possible on a commercial scale; assuming it is proved viable in the pilot projects. If compared to storage in DSF, for which research started almost 30 years ago, then it may be a couple of decades before basalt storage reaches the same level. However some learning from DSF may be applicable to basalt storage, shortening the time for commercialisation.

6. Recommendations

Basalt storage is an active area of research and while not possible in all locations, it may be of significance in regions where this may be the main option for CO_2 storage, therefore IEAGHG should keep updated on developments on basalt storage

Both current pilot projects have not started injection, giving an absence of real-life data; therefore it is recommended that IEAGHG consider further assessment of basalt storage as and when result from the pilot projects become available.

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