IEAGHG Information Paper: 2015-IP1; Impurities in the CO₂ Stream: Effect on the Storage Complex and Well Materials

Progress in our understanding of the effect of chemical impurities on storage complexes and well materials has been communicated in a number of review papers in recent years. Of particular note is the work of Talman (2015) who comprehensively reviews studies concerning the potential geochemical interactions of impurities in saline storage sites and Carroll et al. (2016) who focus on well integrity in CO_2 storage environments.

Geochemical impurities in captured and stored CO_2 arise from two main sources, as part of the injected gas stream and by the interaction of sub-surface constituents. Although capture technologies are generally highly effective at the purifying the CO_2 stream (74.8% - 99.9% pure[1]), existing techniques fail to remove impurities entirely and in many cases pollutants are purposefully stored alongside CO_2 at the same storage site (eg. Acid gas injection across the Alberta Basin and zero emissions processes). Existing sub-surface liquids (eg. Water and hydrocarbons) are 'not so much an impurity as a reality[2]' and have the potential to liberate dissolved gases (methane, hydrogen sulphide etc). These impurities dilute the CO_2 rich phase which may have influences on the physical properties of the injected fluid (eg. Density & Interfacial Tension). Although the CO_2 transport infrastructure already strictly defines impurity limits for CCS projects, research to date has identified a number of possible undesirable geochemical reactions with components in the sub-surface and obviously building a more comprehensive understanding of how these reactions will affect the integrity of storage sites is important.

The aim of this information paper is to condense and broadcast the work of Tallman (2015), Carroll et al. (2016) and others in order to provide a summary of the current state of knowledge in this field and promote the future research recommendations provided by the authors.

1. IMPURITIES AND THE STORAGE COMPLEX

Pure CO_2 streams form weak carbonic acids with the formation water, this induces reactions with rock minerals which neutralise the acid and increase the total dissolved solid content of the water and consequently pure CO_2 is considered to be chemically stable in most geological storage sites in the long term. The introduction of impurities, however, results in complexity due to variations in geochemistry on both a spatial and temporal scale and this makes accurate modelling and simulations very difficult. The various impurities present in CO_2 streams can be partitioned according to their properties and interactions with the storage complex. The most notable geochemical interactions and physical impacts of each of these impurity groups is summarised below.

(a) Acid gases (SO$_x$ & NO$_x$)

The geochemical interactions associated with these impurities are considered to be of greatest concern to CCS projects. Acid gases generally occur in vanishingly small quantities (<100ppmv – 250ppmv) with the exception of some oxyfuel and pre-combustion operations (up to ~2 %). Sulphur oxides (SO$_2$, SO$_3$) are highly soluble in water and so will not migrate with the gas plume and, in relatively short time periods (months), will react with formation waters to produce significant quantities of sulphuric acid (H_2SO_4) resulting in a decrease in pH at the injection zone. This is of course

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[1] Porter, R.T.J., Fairweather, M., Pourkashaniana, M. & Woolley, R. M., 2015, The range and level of impurities in CO2 streams from different carbon capture sources, International Journal of Greenhouse Gas Control, v.36, p.161-174

[2] Talman, S., 2015, Subsurface geochemical fate and effects of impurities contained in a CO2 stream injected into a deep saline aquifer: What is known, International Journal of Greenhouse Gas Control, v.40, pp.267-291

a concern to downhole well materials (discussed in section 2) but may also have implications on cap rock integrity[3] although this is not regarded as a substantial risk since significant volumes of SO_x are not expected to come into contact with the seal. In addition, further oxidation of SO_2 by other impurities will produce sulphates which may precipitate large quantities of anhydrite in carbonate rich reservoirs leading to porosity reductions. This effect may be offset, however, by the potential for SO_2 to improve storage capacity through induced density increase[4]. Nitrous Oxide (NO_x) impurities are thought to behave in a similar way to sulphates producing strong acids with oxidation and hydration but the relative kinetic stability and insolubility of NO_x in water will result in its components and related reactions occurring more diffusely across the aquifer than with SO_x. Consequently NO_x may be more of a concern to caprock integrity, although, because it exists in such low concentrations (<100ppm), there is an absence of research defining the rates or significance of potential reactions[2].

(b) Hydrogen Sulphide (H_2S)

This impurity may be present in the storage formation or as part of the gas stream and at some sites in Alberta is injected at concentrations of up to 84%[5]. The geochemical behaviour of H_2S is strongly dependant on initial conditions in the aquifer, in iron-rich oxidising aquifers, for example, H_2S will react and assist mineralisation of CO_2. In cases where formation waters bear H_2S, extensive H_2S-rich banks will form in the gas plume. The most detrimental effect of H_2S though is that with increasing concentrations, it results in progressively less interfacial tension (IFT) between the water and mixed gases thus degrading the residual trapping ability of the reservoir[6] and therefore reducing storage security. Success of co-injections to date, though, seem to indicate that this effect does not a pose significant risk.

(c) Inert, Non-condensables (O_2, Ar, N_2 and CH_4)

Research thus far indicates that, with the exception of oxygen which increases the reactivity of the gas stream by oxidation reactions and associated acid production (albeit minor in comparison to acid gases), these impurities have no/negligible geochemical effect but do have the potential to significantly reduce the physical storage capacity of the reservoir. In extreme cases where N_2, Ar and O_2 are present at about 15%vol (corresponding to high impurity level oxyfuel combustion), density reductions may reduce storage capacity for CO_2 by over 65%[4]. N_2 and CH_4 are, however, documented to increase IFT thus improving storage security. The trade off, therefore, is that although the injected plume, and therefore monitoring area, will be larger, the residual trapping will occur more quickly so reducing the length of time over which monitoring needs to take place. Another notable point is that Ar and CH_4 are less soluble in water than CO_2 and consequently become chromatographically separated and enriched at the edge of the injection plume and as such may provide the earliest indicator for the arrival of the CO_2 plume which may be relevant to CCS monitoring operations.

Work to date seems to conclude that in all but extreme cases, the impurity regulations set up for transporting CO_2 are sufficient to cover the integrity of geological storage sites but it is clear that there are areas in which future research should be focused. Currently, the greatest area of concern for CCS projects is the post-injection phase in the vicinity of the well and further research in this area is

[3] IEAGHG, 2011, Effects of Impurities on Geological Storage of CO2, Report: 2011/04, 87p

[4] Wang, J., Wang, Z., Ryan, D & Lan, C., 2015, A study of the effect of impurities on CO2 storage capacity in geological formations, International Journal of Greenhouse Gas Control, v.42, pp.132-137

[5] Bachu, S. & Gunter, W.D., 2004, Overview of acid-gas injection operations in western Canada, In: Proceedings of the 7th International Conference of Greenhouse Has Control Technologies, Vol. 1: Peer-Reviewed Papers and Plenary Presentations, Vancouver, BC, September 5-9, 2004.

[6] Iglauer, S., Mathwe, M.S. & Bresme, F., 2012, Molecular dynamics computations of brine–CO2 interfacial tensions and brine–CO2–quartz contact angles and their effects on structural and residual trapping mechanisms in carbon geo-sequestration, v.386 (1), pp. 405-414

recommended, with details of SO_2-H_2SO_4 reactions needing particular attention. In addition it is clear that, although insightful and entirely necessary, numerical simulations and modelling have their limits in such complex chemical systems and data from downhole monitoring should provide very useful information on the true reactivity and behaviour of these impurities. In general improved cooperation between the various research communities involved in this work would help to overcome the complex web of the chemical environments that arise from impure CO_2 injection.

2. IMPURITIES AND THE WELL

Wells provide a direct connection between the CO_2 storage reservoir and the atmosphere and as such present the greatest risk to the permanence of CO_2 storage. Consequently understanding well integrity in sub surface environments relevant to CO_2 storage is of utmost importance. Current understandings on how the two key well components behave in the sub surface, and their potential interactions with impurities, is provided below.

(a) Cement

Despite the complex nature of cement there are surprisingly few mineral phases and related chemical reactions that take place at the CO_2 brine–cement interface[8]. As has already been mentioned, following injection, CO_2 dissolution occurs forming a weak acid with the formation brine. The resulting solution reacts with well cement resulting in well carbonation but the reaction is passivate thus protecting the cement from continued acid penetration and so well cement at a pure CO_2 injection site provides long term storage security. H_2S and SO_2 impurities, which can concentrate around the well, will react with the cement to produce secondary alteration products ettringite and gypsum. These compounds can result in expansion or loss of cohesion of the cement matrix resulting in cracking, pitting and spalling[3] which may, in turn, expose the steel casing to the CO_2 brine. NO_x impurities are also problematic for well cements as NO_2 reacts with water in the formation to produce HNO_3 (nitric acid), this interacts with hydrated cement compounds and unhydrated cement residues, leaching out prevailing Ca ions into solution leaving soft and porous decalcified corrosion material with no binding or protective properties.

(b) Well Casing (Steel)

Well casing will be exposed to formation waters in cases where the cementing is incomplete or corroded. Where unprotected, carbonic acid can result in rapid and destructive corrosion reaching rates of tens of millimetres/year in extreme cases (eg. unpassivated low carbon steel) and, although cement carbonation can help to protect the steel surface by forming iron carbonate scale reducing corrosion rates by a factor of 20, well integrity will eventually be compromised. Impurities which promote decreased pH will serve only to increase the corrosive effect on steel and in cases where oxygen and oxidising acid gases are present well casing will become pitted[7]. Corrosion resistant high molybdenum alloys, corrosion inhibitors and cathoidic protection can be used to prevent corrosion and, combined with adequate cement coverage, will allow for long term storage security[8]. In cases where the storage site is a depleted oil/gas field and legacy wells are used these prevention methods may not be possible.

Current research seems to conclude that the key concern to well integrity in CCS projects is the exposure and therefore corrosion of steel casing by carbonic acid and acid gas impurities serve only to increase this corrosion rate although at new wells preventative measures may be taken to avoid this risk. Well cement is considered to be stable for extensive time frames due to its passivate reaction

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[7] IEAGHG, 2010, Corrosion and materials selection in CCS systems, Report 2010/03
[8] Carroll et al., 2016, Review: Role of Chemistry, Mechanics and Transport of Well Integrity in CO_2 Storage Environments, International Journal of Greenhouse Gas Control, Article In Press

with the CO_2 brine. H_2S and SO_2 impurities may induce ettringite/gysum precipitation although evaluations of the negative impact of these compounds in CO_2 storage environments is unknown. One key area of work which is necessary for better evaluations on sub surface well integrity is a better understanding of the degree to which carbonated cement can protect steel from corrosion in the long term[8]. As Talman (2015) also noted (see above), future research must focus on field/monitoring observations to accompany laboratory/modelling studies as this will provide the most thorough understanding of leakage risks.

CONCLUSIONS:

Research in this field is approaching a more mature stage and it has become clear that in all but extreme cases the CO_2 transport infrastructure limitations on geochemical impurities provide enough coverage to protect the integrity of the storage complex. Well integrity is also considered to be stable in the long term in the majority of cases if the appropriate corrosion protection methods for casing are taken and cementation has been completed to a high standard. This may not be possible at sites with legacy wells and suitable measures to seal these structures will be required. Future research is encouraged to focus on field and monitoring based observations to complement modelling work, with this will come a far more comprehensive and robust understanding of the effect of geochemical impurities on carbon storage.

Alex Rolland
11/01/2016