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Abstract

This report was written as part of task 2.5 the ERA-Net ACT funded ELEGANCY project (271498) and has examined the effects of hydrogen darkening on fibre optical cables for use as downhole monitoring tools for CCS. Darkening of the fibre caused by diffusion of hydrogen in to the cables can render monitoring systems inoperable. In the past, to prevent degradation, coatings have been sometimes applied to the fibre, or the cable enclosed in a sheath but these have not proved particularly effective in preventing hydrogen diffusion over the long time frames requires for CCS. In addition, although most of the common coatings and sheath materials are resistant to dissolved CO_2 data is not routinely supplied about the resistance of these to supercritical CO_2 (SCO_2), so it may be necessary to test the compatibility these coatings and sheaths for compatibility with SCO_2.

With changes in fibre optic cable manufacturing processes combined with the use of high quality PSC, in combination with hermetic coatings many manufacturers claim that fibres that meet ITU-T G.652.D standard, suggesting that with the use of high quality fibres and coatings, that hydrogen darkening can be prevented under conditions expected in a typical CCS site. However, it should be cautioned that there is little or no data about the long-term performance of such cables exposed to either dissolved CO_2 or SCO_2, and it may be necessary to test the compatibility these cable assemblies for compatibility.

TABLE OF CONTENTS

Page

1 INTRODUCTION

In Work Package 2 of the ELEGANCY project, several activities are underway to investigate the physical, chemical and biological properties of the fluid and rock environment of carbon dioxide storage reservoirs and the influence hydrogen will have on them. Amongst these activities is the review of the effects of hydrogen on fibre optic cables installed as part of a sensor and monitoring network. It is well known particularly from deployment in geothermal systems (Lemaire, 1991, Mendez and Morse, 2007, Stone, 1987) that fibre optic cables exposed to hydrogen can suffer degradation of the optical properties, so called ‘hydrogen darkening’. This report represents a review of the available literature and provides recommendations for minimising the effects of hydrogen darkening in monitoring systems for the operation of a CCS storage site. Though some fibre optic based installations have been deployed/tested at CCS sites there is little information about their long-term performance. In the case of CCS, the hydrogen gas may be present naturally in the reservoir formation, be generated by microbial or chemical reaction (see ELEGANCY deliverable, D2.5.1 *Hydrogen in subsurface environments and response of microbes*) or even be present as an impurity in the injected CO_2 stream.

The problem is particularly relevant to fibre optic cables are used for distributed temperature sensing (DTS). The darkening of the fibre can distort the DTS reading and possibly even render the DTS system inoperable. The rate of degradation is a function of H_2 concentration, exposure time and temperature. To prevent degradation, coatings are sometimes applied to the fibre, or the cable is enclosed in a sheath. This report examines if fibre degradation will be an issue in a CCS storage site, in addition, it will review the effectiveness/durability of coatings and sheaths in the acidic environment associated with dissolved CO_2.

1.1 Hydrogen darkening

Fibre optic cables are based on silica glass, often with cores, doped with additional elements (e.g. germanium, phosphorus, neodymium, ytterbium) to provide enhanced performance. As the light (typically a laser source is used to provide a pulsed light) travels through the fibre, it undergoes scattering even in the absence of any structural defects in the fibre or the presence of impurities. Most of the scattering is of the same wavelength as the illuminating laser light (Rayleigh scattering, (Andrews, 1999) and is caused by structural variations in the fibre itself. A smaller component of the scattering is known as Raman scattering (Andrews, 1999), which occurs at different wavelengths to the illuminating light. The degree of scattering is a function of temperature, some of this light is backscattered, and it is this backscattered light that is used for distributed temperature and pressure measurements. Light propagation and the associated backscattering is very responsive to environmental changes and so fibre optic sensors are not only extremely sensitive but also have fine spatial resolution, for example various systems are available with (claimed) spatial resolution of 10’s cm together with a temperature accuracy of ±0.5°C.

Typically, a fibre optic cable is made up of several parts (Figure 1) a central core (generally doped to provide enhanced performance) is surrounded by a protective outer silica cladding and the fibre is then coated with one or more coatings to prevent mechanical damage, and water ingress. Coatings may be polymeric, metallic or carbon depending on the application. Some coatings are to varying degrees permeable to hydrogen gas, and this can then penetrate the silica glass through to the central core, causing attenuation in the infrared part of the spectrum, which is key to the operation of fibre optic based sensors. Hydrogen maybe present naturally in the groundwater, or may be the result of chemical and/or microbial interactions in the borehole and surrounding rock, and in the case of a CCS storage site may be present as an impurity in the injected CO_2 stream.

Additionally, if the fibre optic cable is encased within a steel tube, degradation of the oils used in the manufacturing process may also be a source of hydrogen. Indeed, in geothermal wells where fibres that have been degraded and have been replaced but have reused the same steel tubes then these fibres performed better (Normann, *et al* 2001).

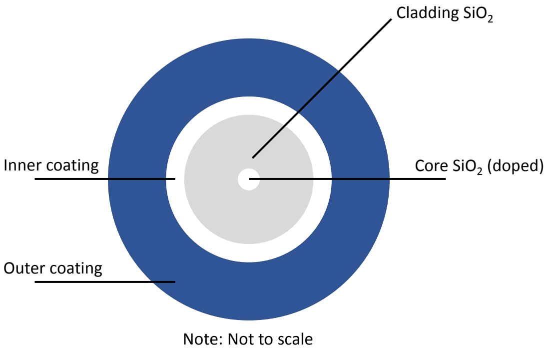

Figure 1 Schematic of typical optic fiber

The diffusion rate of hydrogen into the silica glass is rapid ($D_{H_2} \approx 1.2 \times 10^{-11}$ $cm^2.s^{-1}$, at 20°C, (Stone, 1987), and exposure of just a few hours (Lemaire, 1991) is enough to cause significant degradation. The diffusion also increases with temperature though the degree of absorption falls off with increasing temperature. Losses in light transmission, can reach maximum levels within 2 weeks (Mendez and Morse, 2007). This degradation of the optical properties is commonly referred to as ‘hydrogen darkening’. The nature of this can take two different mechanisms, the first being reversible gas absorption (Lemaire, 1991). This is more common at low temperatures, <200°C (Yu *et al*, 2016) in which molecular hydrogen is physically dissolved in to the silica glass, having diffused into it. If the source of the hydrogen is removed then this dissolved hydrogen can diffuse back out of the fibre (Stone, 1987, Lemaire, 1991), and the effects may be reversed, the rate of recovery is similar to the rate of attenuation with 95% of the hydrogen diffusing out of the silica glass fibre in two weeks at room temperature following removal from the hydrogen source (Mendez and Morse, 2007).

At higher temperatures, attenuation is attributed to chemical reactions within the glass network, usually by the formation of hydroxyl groups. Unlike the simple dissolution of hydrogen, this hydroxyl formation is accumulative, and non-reversible. It is thought that the reactions tend to occur at defect sites within the silica glass and that the attenuation will increase until all such defect sites have reacted, doping of the silica glass and/or impurities present can enhance the degradation. It should be noted that this degradation is not confined to the fibre optic cables but also to optical fibre Bragg gratings (Martelli *et al* 2011) used as passive, active or sensing devices.

A less common type of reaction, which occurs even under ambient conditions, ensues if there is alkali (i.e. Na, Li, K) contamination in the fibre, even contamination of the order of a few ppm can result in attenuation of the light signal over time (Mendez and Morse, 2007). The alkali contamination can be present in the original quartz starting material or due to insufficient purification during manufacture of the silica fibre.

Although the mechanisms of the hydrogen diffusion and or reaction with the silica glass are different the ultimate effect is the same – degradation of the optical properties of the fibre, and all are collectively referred to as ‘hydrogen darkening’.

In case any, diffusion of hydrogen into the silica glass, and in particular the inner core, causes attenuation of the light and subsequent reduction in the performance of the fibre optic cable sensor, used for monitoring. Figure 2 (Taken from Mendez and Morse, 2007) shows an example of the degree of degradation of the light in a typical fibre due to hydrogen ingress.

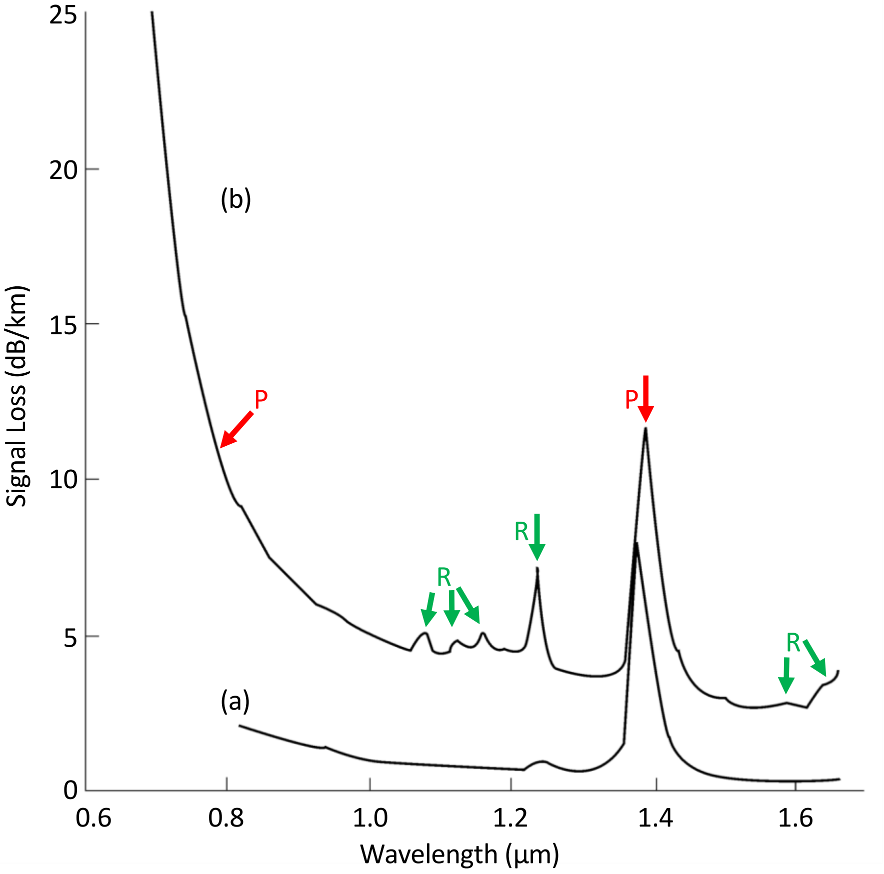

Figure 2 Example of typical Hydrogen losses before (a) and after (b) exposure to H_2 *at 150°C for 3 days. Loss features labeled ''R'' are reversible, loss features labeled 'P' are permanent. After Mendez and Morse, (2007).*

1.2 Prevention of Hydrogen ingress

Various methods have been developed to prevent or slow down hydrogen ingress, essentially this entails either coatings being applied to the outer surface of the silica glass, or changes in the nature (quality) of the silica glass used in the manufacture of the fibre cable.

1.2.1 Coatings

Many fibres have jackets made from plastics (e.g. polyimide, PVC) or silicon, sometimes over an inner made from stainless steel, or simply stainless steel itself. However as noted above, steel corrosion can itself cause hydrogen generation, and may also be unsuitable for use in a CSS site due to corrosion as a result of acidity of the groundwaters caused by dissolution of the injected CO_2. Most of the other materials are resistant to dissolved CO_2 but commonly data is not routinely supplied by the manufacturers about the resistance of these to supercritical CO_2 (SCO_2), so it may be necessary to test the compatibility these coatings to SCO_2.

Whilst these jacket materials have varying degrees of chemical and physical resistance many of the plastics, whilst able to prevent water ingress, are permeable to hydrogen and so other solutions have been developed to reduce hydrogen diffusion.

One method is to coat the fibre with a hermetic coating, for example carbon. By applying multiple layers of carbon during the fibre drawing process a hydrogen resistant seal can be achieved (Mendez and Morse, 2007). Indeed, manufactures such as Corning claim that fibres that are manufactured to be compliant to the ITU-T G.652.D (International Telecommunication Union) standard (i.e. Corning's SMF-28e® and NexCor™ fibres), exhibit a low attenuation increase due to hydrogen aging (see Jacobs 2004). However, hydrogen can still diffuse through the carbon layer over time and the rate increase with temperature. At room temperatures depending on the nature of the carbon coating, the rate of hydrogen diffusion can be below detection (Mendez and Morse, 2007). However, at higher temperatures and pressures the carbon coating loses it hermeticity, thus carbon coated fibres are best used at temperatures below ≈ 170°C. Most CCS sites are likely to below this temperature, so this may be sufficient protection for the fibre optic cable to prevent the effects of hydrogen ingress but as with other most of the other materials no data has been found about the resistance of these to supercritical CO_2 (SCO_2), so again it may be necessary to test the compatibility of these carbon coatings with SCO_2.

1.2.2 Silica quality

An alternative solution to the problem of hydrogen diffusion is to examine the nature of the fibre itself, and in particular the design of the fibre core. The silica composition affects the solubility of any dopant added which, will in turn affect the optical properties of the fibre. These quantities affect the ultimate suitability of the optical fibre's resistance to hydrogen darkening. Key to this is the minimisation of defects in the silica glass structure, either caused by the manufacturing process or the addition of dopants, to the central core, such as germanium (to raise the refractive index of the core) and phosphorus (use to control the viscosity of the glass). Both Ge and P are known to increase the number of defects in the silica (Stone ,1987) leading to greater susceptibility to hydrogen diffusion. Most of the glass in a typical fibre is the outer silica cladding, the physical properties of this 'optically inactive' glass are dependent on the materials and the manufacturing process.

It has been reported by Bell et al (1962) that fibres produced by fusing natural quartz crystals can contain metastable OH impurities, which may over time convert to more mobile hydrogen species which can then diffuse through the silica glass. If such fibres are hermetically sealed with, for example, carbon coatings then any internally produced hydrogen can diffuse into the core.

Using a higher quality silica particularly for the core can help alleviate these effects. This can be used with a fluorine doped silica making up both the core and cladding. This type of fibre is sometimes referred to as 'pure silica core (PSC)' and has fluorine as the only dopant. Normann *et al* (2001) have suggested that this combined with a carbon coating may be the optimum solution for deployment in Geothermal systems.

2 CONCLUSIONS AND RECOMMENDATIONS

This report has examined the effects of hydrogen darkening on fibre optical cables for use as downhole monitoring tools for CCS. Darkening of the fibre can distort for example the DTS readings and even render such systems inoperable. In the past, to prevent degradation, coatings have been sometimes applied to the fibre, or the cable is enclosed in a sheath but these have not proved particularly effective in preventing hydrogen diffusion over the long time frames requires for CCS. In addition, although most of the common coatings and sheath materials are resistant to dissolved CO_2 data is not routinely supplied (if available at all) by the manufacturers about the resistance of these to supercritical CO_2 (SCO_2), so it may be necessary to test the compatibility these coatings and sheaths for compatibility with SCO_2. Although the maximum recommended temperature for the effective use of carbon coatings (≈170°C) is higher than many proposed sites for CCS, even at low temperatures carbon coated cables may susceptible to damage from very long-term exposure to hydrogen, and it may be prudent to consider additional measures.

With changes in fibre optic cable manufacturing processes combined with the use of high quality PSC, in combination with hermetic coatings many manufacturers e.g. Corning claim that fibres that meet ITU-T G.652.D standard (i.e. Corning’s SMF-28e$^{\circledR}$ and NexCor^{TM} fibres, Jacobs 2004), will have stable long term performance. Other manufacturers e.g. Silixa (*pers comm*) make similar claims, suggesting that with the use of high(er) quality fibres and coatings, that hydrogen darkening can be prevented under conditions expected in a typical CCS site. Thus, it would seem that manufacturers, at least for other industries (i.e. Geothermal) are confident that hydrogen darkening can be minimised, though it should be cautioned that there is little or no data about the long-term performance of such cables exposed to either dissolved CO_2 or SCO_2, and it may be necessary to test the compatibility these cable assemblies for compatibility.

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