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SEASONAL STORAGE OF HYDROGEN IN A DEPLETED NATURAL GAS RESERVOIR

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2

3   Abstract

4   Hydrogen storage in a depleted gas reservoir or in an aquifer offers the potential for the seasonal storage of inherently variable

5   renewable energy, by the electrolysis of water during periods of excess energy production. Here we investigate whether such

6   storage is technically feasible.

7

8   We compared the respective capacities and deliverabilities of hydrogen to established natural gas in a seasonal storage facility,

9   on the basis of an estimated total volumetric capacity of 48MMm^3, delivery pressures between 5-10MPa and emptying period of

10   120 days for the Rough Gas Storage Facility (UK). For the modelled scenario, an average power in the order of $4 - 5$ GW would

11   be required during a six month injection cycle to fill the reservoir to capacity. The equivalent hydrogen facility could store and

12   supply 42% of the energy capacity supplied by its natural gas counterpart, and for an emptying period of 120 days could deliver

13   power at an average rate of approximately 100 GWh/day, or ca. 40% of the energy deliverability of natural gas.

14

15   There appears to be no insurmountable technical barrier to the storage of hydrogen in a depleted gas reservoir. Hydrogen losses

16   from dissolution and diffusion could be reduced to less than 0.1%. Losses from biological conversion of residual CO_2 were

17   limited even with calcium carbonate dissolution. However, the biological reduction of sulphur minerals to hydrogen sulphide

18   remained a potential problem.

19

20   1   Introduction

21   The deployment of renewable energies on a scale required for decarbonisation of the energy systems will impose seasonal

22   variations on the supply over which operators will have no control. For example, in the Scandinavian and Baltic area, the monthly

23   average wind speed at a given time of year can vary by more than 20% from one year to the next at one given location [1]. The

24   variability of annual mean values for wind speed were also found to vary between 3 and 7% depending on the site, which led to

25 estimated variations of between 8 and 18% for the energy output from wind turbines at these locations [1]. In this context, large

26 scale, 'seasonal' storage could be very helpful to alleviate shortfall of energy outputs during certain weeks, months or even

27 perhaps in a lean year.

28

29 Hydrogen is one option which combines versatility of applications (power, heat, transport and chemical feedstock) with a high

30 density of stored energy suitable for long term storage. Currently, it is mostly produced by reforming of natural gas with an

31 energy efficiency of 65-85% [2]. However, it can also be produced directly from renewable power by electrolysis of water, which

32 is the splitting of water into hydrogen and oxygen in electrochemical cells, with an energy efficiency in the range 55-75%

33 depending on the capacity factor (i.e., operating at lower load will increase energy efficiency but require more electrolyser

34 capacity, hence more capital costs) [2,3]. One electrolysis technology in particular, alkaline electrolysis, is considered to be fairly

35 mature, having been deployed in industry for hydrogen production [4]. In alkaline electrolysis, the electrolyte is a concentrated

36 solution of potassium hydroxide (KOH) at 28% wt., for which the conductivity is adequate for temperatures in the region 80-

37 120 °C (depending on the pressure at which the electrolyser operates). The electrodes are typically based on Raney nickel rather

38 than costly precious metals, which is advantageous. A notable development in more recent years is the optimization of

39 electrolysis that can nearly instantly follow the load (i.e. the power supply), making it particularly suited to the use of renewable

40 power from sources like wind, marine or solar energy [5, 6]. In addition, operating under pressure also has the advantage of

41 producing a gas that is already pressurized to a certain extent (up to 30 bar), which simplifies any subsequent processing and

42 storage steps by removing the need for several stages of compression, as well as requiring smaller compressors (the pre-

43 compressed feed is more compact) and consuming less power [5, 6].

44

45 While the gaseous form of hydrogen is often seen as presenting a challenge for its storage on a large scale, it is encouraging that

46 a similar requirement for seasonal storage is currently met for natural gas by underground storage in natural reservoirs. A total

47 of 688 natural gas storage facilities were operated worldwide as of January 2013, with a combined working gas capacity of 377

48 billion m^3, or 10% of the world consumption (2012 figures, [7]). The 'working gas capacity' of a storage reservoir is defined as

49 the total amount of gas that can be made available to customers, and is one of the two main operational specification of a reservoir.

50 The other major characteristic of a reservoir is the deliverability rate, i.e. the rate at which the gas can be withdrawn from the

51 reservoir. The working gas capacity (WGC) excludes the cushion gas capacity, which represents the volume of gas that must

52 remain unextracted as buffer for reservoir management purpose and for providing the minimum pressure required for meeting

53 the specified deliverability. The main types of reservoirs include salt caverns, aquifers and depleted natural gas or oil reservoirs.

54 Salt caverns typically present smaller working gas capacities but greater deliverabilities than depleted reservoirs or aquifers,

55 contributing worldwide only 7% of the total WGC and 14% of the sites, and yet 22% of the total deliverability (2012 figures,

56 [7]). Depleted natural gas reservoirs are by far the most common amongst these, accounting for 74% of the total number of sites

57 [7]. They have the economic advantage over aquifers of providing cushion gas capacity with their residual native gas.

58

59 For example, the Rough Gas Storage Facility (RGSF) is a partially depleted natural gas reservoir in the Southern North Sea,

60 about 18 miles off the coast of Yorkshire, England. It is used to supply natural gas on the UK grid at times of peak demand. With

61 up to 4.7 billion m^3 capacity, the volume of natural gas made available represents 9 days of supply, and it can be extracted at a

62 rate that matches 10% of the UK's peak gas demand [8]. In view of their large capacities and the existing data and experience

63 from natural gas, similar types of reservoirs could be considered for seasonal hydrogen storage.

64

The idea was initially explored in the 1970's when economies were embracing nuclear and renewable energies as alternatives to fossil fuels, but the body of literature that is available is limited. A preliminary assessment by Carden and Paterson [9] concluded that there were "no unsurmountable physical or chemical problems associated with underground hydrogen storage in sedimentary formations". In particular, the authors provided an initial estimate of the losses of hydrogen to dissolution in the surrounding underground water and further diffusion (including into the water saturated pores of the caprock). Pichler [10] suggested that these estimates be corrected, by including the influence of pressure and salinity on the solubility of hydrogen in water, as well as replacing the pure diffusivity with an effective diffusivity that took into account the constriction and tortuosity of pores. This author then concentrated on evaluating the chemical interactions of the hydrogen with the surrounding minerals in the reservoir. Panfilov [11] modelled the population dynamics of bacterial growth that is known to feed on hydrogen and carbon dioxide to produce methane in some reservoirs, coupled with the reactive transport of these gases in the reservoirs. His work evidenced a possible mechanism for the observed segregation of hydrogen-rich and methane rich areas in the aquifer town gas storages of Lobodice (Czech Republic) and Beynes (France).

In the UK, salt caverns would have great potential for hydrogen storage onshore for the purpose of daily load-following operations, on a decarbonised electricity grid that relied on electrolysis, or other methods for producing hydrogen like reforming and gasification for capturing CO_2 from fossil fuels. However, the total energy stored would be in the few 100's of GWh (150 GWh_e is suggested in [12]), which compares with about 40 TWh as available from the Rough Gas Storage Facility [8] and hence significantly short of the mark for seasonal storage. Generally, the lack of suitable depleted gas reservoirs onshore for seasonal storage suggests that storage should be done offshore, where many natural gas reservoirs are nearing the end of their productive lives. Public opinion might also favour storage in an offshore setting.

This paper is a preliminary assessment of the feasibility of storing hydrogen in the same type of reservoirs once commercial extraction of their natural gas has ceased, with emphasis on the storage characteristics as expressed in total energy stored ('working gas capacity') and rated capacity of supply ('deliverability'). We also checked the potential impact of the chemical and biological stability of the hydrogen and re-evaluated an upper bound for the losses from dissolution and diffusion in the reservoir.

2 Methodology

The Rough Gas Storage Facility was chosen as a well characterised model example for this preliminary study. The following average values were taken for the conditions inside the reservoir: Depth below the sea bed, 2743m; Temperature, T = 365K; Initial pressure, 31.3 MPa, as indication of the maximum pressure that the reservoir could withstand; main material was sandstone of porosity φ = 0.2 and permeability to methane 75 mD (or $7.4 \cdot 10^{-14}$ m^2).

More generally, the reservoir was assumed to have a structure and composition similar to the majority of those found in the UK southern North Sea basin, i.e. clay-bearing sandstone reservoirs with a varying proportion of carbonates present as cements (from less than 1% to up to 24%) [13], topped by a non-porous cap rock made of evaporite (anhydrite or rock salt) or sometimes shale.

102 The total capacity for natural gas was V_S = 48 MM m³ (or 48·10⁶ m³), as estimated with the following relationship:

103

104 $$V_S = V_R \varphi (S_g - S_{gr}) \qquad (1)$$

105

106 where V_R the rock bulk volume (i.e. the reservoir geometric volume), S_g the volume fraction of pore space occupied by gas, and
107 S_{gr} the irreducible gas fraction that practically remains when all gas has been extracted to the extent that the delivery flowing
108 pressure is at the minimum that is allowable. We assumed that the energy that drove the gas out of the reservoir came from its
109 sole expansion.

110

111 The amount of hydrogen that could be stored in the reservoir was expressed as

112

113 $$\frac{V_G^H}{V_R} = y_H \varphi (1 - S_{wi}) \frac{P}{ZP_o} \frac{T_o}{T} \qquad (2)$$

114

115 where V_G^H is the total capacity for hydrogen, y_H the volume fraction of hydrogen in the gas, S_{wi} the irreducible water saturation
116 (i.e. the fraction of water that remains in the pore volume when gas is stored), estimated at 0.2 in this reservoir. P and T are the
117 reservoir temperature and pressure, respectively, Z the compressibility, and P_o and T_o are the temperature and pressure at standard
118 conditions (1 atm and 273K, respectively).

119

120 Hydrogen was produced by alkaline electrolysis, and compressed to injection pressure between 5 and 10 MPa.

121

122 Fundamental physical properties of natural gas and hydrogen that are relevant to this study are reported in Table 1, with methane
123 chosen as the model compound that represented natural gas. Gas pressure, temperature and specific volume were linked together
124 by an equation of state for the gas under consideration (hydrogen or methane), which was following the Soave, Redlich and
125 Kwong model [14]. This model fitted the values reported in the literature for Z which are displayed in Table 1.

126

127 Table 1: Physical properties of hydrogen and methane. Figures were taken or interpolated from data in [15] and [16] within
128 appropriate ranges of conditions. The influence of moisture was also considered regarding viscosity using the Gorning-Zipper
129 formula [17] at reservoir pressures and at water vapour saturation for the reservoir temperature, and it was found to be negligible.

	γ_g, relative gravity at standard conditions (air=1)	Enthalpy of combustion at standard conditions, ('Lower Heat Value') MJ/kg	Z, compressibility factor	Dynamic viscosity μ, kg m⁻¹ s⁻¹
Methane	0.555	50.0	0.987 at 5MPa, 365K; 0.942 at 10MPa, 365K.	$1.40 \cdot 10^{-5}$ at 5MPa, 365K; $1.51 \cdot 10^{-5}$ at 10MPa, 365K.
Hydrogen	0.0698	120	1.03 at 5MPa, 365K; 1.05 at 10MPa, 365K.	$1.01 \cdot 10^{-5}$ at 5 − 10MPa, 365K.

				at 10MPa, 365K.

2.1 Chemical stability of the hydrogen in the reservoir

Possible reactions between hydrogen and the mineral components of the reservoir were investigated using *Phreeqc*, a software for aqueous geochemical modelling that was developed by the US Geological Survey. The software is made freely available on the USGC's website, www.usgs.gov. As a minimum, the model is able to predict the thermodynamic stability of the rock and gas in the presence of water. No change reliably indicates that a reaction will not occur. However, a change suggests that transformations might occur, provided that the kinetics allow them to proceed. Kinetic data may be required at that stage as input to the model.

Several 'assemblages' of minerals were investigated for thermodynamic stability, all in the presence of water and hydrogen. Any gaseous or dissolved reaction products had to be included in the list, since reactions will be equilibrium limited and hence potentially limited by concentrations of gas products. The starting point always included at least one mol of hydrogen and 1 kg of water, as well as 1 mol of each of the minerals present in a given assemblage, and 0 mol of any gas product (e.g. CO_2, methane or hydrogen sulphide).

Firstly, we examined a mixture of

- Sandstone, including quartz SiO_2; illite $K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$; kaolinite $Al_2Si_2O_5(OH)_4$; chlorite $Mg_5Al_2Si_3O_{10}(OH)_8$; montmorillonite $Ca_{0.165}Al_{2.33}Si_{3.67}O_{10}(OH)_2$; sepiolite $Mg_2Si_3O_{7.5}OH : 3H_2O$; K-feldspar $KAlSi_3O_8$; K-mica $KAl_3Si_3O_{10}(OH)_2$; anorthite $CaAl_2Si_2O_8$; albite $NaAlSi_2O_8$.
- Iron oxides, including hematite Fe_2O_3 and goethite $FeO(OH)$;

This choice was made on the basis that the vast majority of gas reservoirs in the North Sea are primarily made of clay-bearing sandstones, with iron oxides cements [10, 13].

The following assemblage was also examined in the presence of water, hydrogen and hydrogen sulphide:

- Sulphur-containing minerals, including: anhydrite $CaSO_4$; gypsum $CaSO_4 : 2H_2O$; pyrite FeS; sulphur S.

This time, the rationale for this choice was based on the usual presence of H_2S in natural gas (hence in the residual gas), as well as sulphates (of which anhydrite and gypsum are frequent representatives), pyrite and sulphur minerals in the reservoir. The conversion of hydrogen to H_2S by sulphate reducing bacteria is well known in the oil and gas industry, and a major operational

167 inconvenience and hazard. Even if H_2S is not initially present, it could in principle be generated from sulphur-containing minerals
168 in the presence of hydrogen if the Gibbs enthalpies of the corresponding reactions are negative at appropriate conditions of
169 temperatures and pressures.

170

171 Finally, the following assemblage was investigated in the presence of water, hydrogen, carbon dioxide and methane:
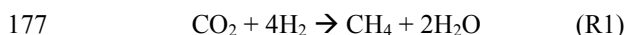
172

173 - Carbonates, including: calcite $CaCO_3$; dolomite $MgCa(CO_3)_2$; and siderite $FeCO_3$,

174

175 the reason for considering this assemblage being the Sabatier reaction,

176

177 $$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \text{(R1)}$$

178

179 with CO_2 either present in the residual natural gas or supplied by the carbonates in the rock if acidification occurred (e.g. as a
180 result of biological activity).

181

182 **2.2 Biological consumption of hydrogen in the reservoir**

183

184 It is known that micro-organisms of the *Archaea* domain are able to live in reservoirs, including methanogenic bacteria [18,19]
185 and sulphate reducing bacteria [19, 20], as well as the type of bacteria that are used by the mining industry for the lixiviation of
186 metallic ores [19, 20]. All of these can feed on hydrogen, and in many cases can modify the composition of the gases present in
187 the reservoir. Whenever the thermodynamics of the assemblage allow it and temperature and salinity are not so extreme as to
188 prevent even the most extremophile of these micro-organisms to thrive [19], it can be assumed that their activity is likely, and in
189 some cases may result in hydrogen loss or the creation of difficult contaminants in the hydrogen gas product.

190

191 In the event of thermodynamically unstable assemblages involving sulphur being identified, the likelihood of bacterial presence
192 would suggest not to proceed with storage unless perhaps desulphurization units from prior natural gas extraction activities were
193 still available and fit for purpose with respect to handling the hydrogen-rich product stream.

194

195 The consequences would be expected to be less critical when identifying thermodynamically unstable assemblages involving
196 carbonates. The main effect would be a loss of product and a change in composition. There is at least one documented instance
197 of a town gas stored in a holding tank which had its composition significantly affected by conversion of hydrogen to methane
198 by bacterial action [21]. In addition, (R1) indicates a reduction in the number of moles, hence a loss of pressure in the reservoir,
199 which would affect recovery and energy efficiency of the process.

200

201 In these conditions, we sought to estimate an upper limit to the effect of this microbial activity on the reservoir and the stored
202 hydrogen inventory, assuming a starting concentration of CO_2 at the maximum possible value in the gas phase ($y_{CO2} \sim 1$; noting
203 that this value would typically be less than 2% in the UK southern North Sea basin); and a maximum reservoir pressure of 10MPa
204 with no subsequent injection of CO_2 and unlimited amounts of carbonate minerals available for CO_2 evolution.

205

206 A choice of a value for the pH for the estimate required care, as acidification could result from both the dissolution of hydrogen
207 and biological activity (including by direct oxidation of hydrogen to H^+ ions, which is a known metabolic pathway for energy
208 production of some of these bacteria), and acidification in turn would affect microbial growth and release of CO_2 from carbonate.
209 A constant value of 5 was chosen for the pH, consistent with maximising the release of CO_2 from carbonates while being a
210 typical lower threshold for the growth of methanogenic bacteria (see for example [22]).

212 Having set the environmental conditions, the *Phreeqc* model was used to predict the final outcome of the reactions regarding the
213 total availability of CO_2 from carbonate. In particular, the ability of the carbonate rock to maintain a significant dissolved CO_2
214 concentration was affected by the accumulating calcium ion in the water, and when a limiting value of $[Ca^{2+}]$ was reached the
215 only source of CO_2 would be that present in the gas phase. At pH = 5, the *Phreeqc* model predicted this value to be $[Ca^{2+}]_{lim} =$
216 0.26 mol/L.

218 Finally, quantifying the utilisation of hydrogen for microbial growth and methane production required writing an elemental
219 balance for bacterial growth, as well as ascribing a value for the ratio of the rate of biomass production rate to that of methane.

221 When considering a typical experimental value of 40 % by weight of carbon, 43% for oxygen, 11% for nitrogen and 6% for
222 hydrogen for dry methanogenic cells [23], an elemental formula of $CH_{1.8}O_{0.8}N_{0.24}$ was arrived at for the dry cell. Individual cells
223 were assumed to be spherical with a diameter of ca. 1.5 μm [22], i.e. a live cell mass m_c of about 1.77 pg, with a typical value of
224 70% for the water content of living organisms. In these conditions, the overall stoichiometry for the production of biomass was

226 $CO_2 + 2.1H_2 + 0.12N_2 \rightarrow CH_{1.8}O_{0.8}N_{0.24} + 1.2H_2O$ (R2)
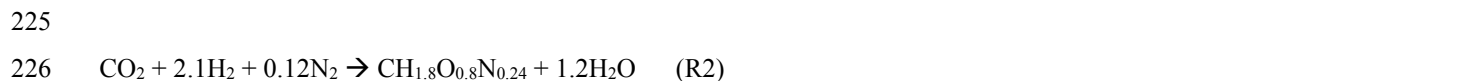
228 where CO_2, N_2 and H_2 were assumed to be the sole sources of carbon, nitrogen and hydrogen respectively; R1 was the only
229 significant source of energy for the cells; and waste products other than water (and also methane in R1) are being neglected.

231 In this paper, a realistic value for the yield of microbial biomass with respect to methane production $Y_{X/CH4}$ was taken as $5 \cdot 10^{12}$
232 cells / mol methane [22]. Given the figures given in the previous paragraph, this translated into the assimilation of 3.5 g carbon
233 into microbial biomass for every mol (i.e. 16 g) of methane produced as per (R1). Hence a full balance per mol of methane
234 produced,

236 1 + 3.5/16 = 1.22 mol of CO_2 utilised;
237 4 + 2.1x3.5/16 = 4.46 mol H_2 utilised;
238 0.12x3.5/16 = 0.026 mol N_2 utilised;
239 for every mol of methane produced,
240 with the co-production of 0.22 mol of biomass on the basis of 1 mol C in its elemental formula.

242 In particular, these figures allow to estimate for the ratio of utilisation of hydrogen to CO_2 a value $Y_{H2/CO2} = 4.46 / 1.22 = 3.66$.

7

244 The maximum possible loss of hydrogen expressed as a proportion of the total hydrogen stored in the reservoir could then be
245 calculated as

246

247
$$L_b = Y_{H2/CO2} \frac{y_{CO2}P(1 - S_{wi}) + ZRT(C_o + [Ca^{2+}]_{lim})S_{wi}}{y_H P(1 - S_{wi})}$$

248

249 (3)

250

251 where C_o was the initial and equilibrium concentration of CO_2 in the liquid; y_{CO2} and y_H the molar fractions of CO_2 and hydrogen
252 in the gas phase (resp.); $S_{wi} = 0.2$ was the irreducible water concentration left in the pores when gas is stored,.

253

254

255 **2.3 Leakage of hydrogen from the reservoir**

256

257 Natural gas reservoirs have held their contents for millions of years before human exploitation began, and therefore it could be
258 possible that the same geological formations may be able to keep hydrogen contained for seasonal storage. However, due to
259 hydrogen having a greater diffusivity than methane, it is required to estimate the scale of its loss through the underlying aquifer
260 and the cap rock above. Leakage of free-phase gas through faults or fractures was neglected since this was considered to be
261 normally absent from natural reservoirs.

262

263 Instead, dissolution of gas in the water that occupies the pores of the cap rock and also the underlying aquifer was considered.
264 Oil was neglected in this study, given that it is not a significant component in gas reservoirs that are found in the Southern North
265 Sea. Applying Fick's laws of diffusion to the hydrogen diffusing away from a reservoir of average thickness H and area A, the
266 amount of hydrogen V_{dH} (expressed in Nm³) that has diffused away from the reservoir through an area A after a period of time t
267 is [24]

268

269

270
$$\frac{V_{dH}}{A} = 2S_H \sqrt{\frac{D_e \varphi_d t}{\pi}} \qquad (4)$$

271

272 where S_H is the dissolved hydrogen concentration in the reservoir at saturation at T and P (i.e. the solubility in Nm³/m³); D_e the
273 effective diffusivity; and φ_d the porosity of the interface (caprock or aquifer).

274

275 When comparing this number with the initial inventory of hydrogen in the reservoir, the fraction of hydrogen lost by dissolution
276 and diffusion through the cap rock or aquifer after a time t was

277

278
$$L_d = \frac{2S_H \sqrt{D_e \varphi_d t / \pi}}{y_H \varphi(1 - S_{wi}) \frac{P\, T_o}{ZP_o\, T} H} \qquad (5),$$

279

280

281   We assumed that $\varphi_d = 0.2$ for the aquifer (i.e. the same as for the reservoir, for which the value was previously stated) and $\varphi_d =$

282   0.05 for the cap rock. Values for S_H in pure water at the reservoir conditions of temperature and pressure were taken from [25].

283   Since salinity will have a detrimental effect on hydrogen solubility [10], we expect the result from Equation (5) to be an

284   overestimate.

285

286   The effective diffusivity can be modelled as [26]

287

288    $$D_e = \frac{D_H \varphi_d \delta}{\tau} \qquad\qquad (6)$$

289

290   where D_H is the diffusivity of hydrogen in water, δ the constriction factor of the pores and τ their tortuosity.

291

292   δ is typically equal to 1 given that the pores are at least two orders of magnitude larger than the gas molecules. In addition, τ can

293   be estimated from the porosity through $\tau = \varphi_d^{1-m}$. The value of the cementation coefficient m was estimated at 2 in the aquifer

294   and 1.7 in the cap rock [27 – 29].

295

296   **2.4 Operation of the reservoir for hydrogen storage**

297

298   Operation of the reservoir for hydrogen storage was considered from the point of working gas capacity and deliverability and

299   emptying period, as well as losses as estimated by the methods that were previously introduced.

300

301   However, we first must discuss the potential impact of impurities from the reservoir. A depleted natural gas reservoir contains a

302   residual proportion of gas within the pore space, at least the residual saturation (S_{gr}) and probably more depending on the

303   economics of the field when it was abandoned. As this phase will be miscible with the injected hydrogen, it is reasonable to

304   expect that during the initial cycles of hydrogen storage, the recovered hydrogen will contain a proportion of natural gas, which

305   will decrease with the number of storage cycles. However, the degree up to which native and injected gases will mix is uncertain.

306   Experience with natural gas storage demonstrated a low degree of mixing between native and injected natural gases. Piston-like

307   behaviour of the injected gas phase has been observed [30], but the same remains to be proven for hydrogen.

308

309   The contaminants that could diffuse into the stored hydrogen are those we would expect to find in natural gas, i.e. chiefly methane

310   with traces of other hydrocarbons, as well as traces of carbon dioxide, nitrogen and hydrogen sulphide. Depending on the

311   concentration of these impurities and the final use of the hydrogen, purification of the hydrogen may or may not be required

312   before injection back into a transmission or distribution pipeline. For example, methane is unlikely to cause concern, but H_2S

313   could damage fuel cells that were powered by the contaminated hydrogen. In his study we assumed that contamination was not

314   a serious concern based on the observed limited extent of mixing between residual and stored gas in the Rough Gas Storage

315   Facility, and the lack of negative impact from the majority expected contaminant, methane.

316

317 As mentioned in the introduction, cushion gas must always remain in the reservoir to ensure delivery out at a pressure P_f

318 without requiring extensive recompression of the gas before processing and transmission. The volume of this gas is referred to

319 as the Cushion Gas Requirement (CGR). The total gas volume of the reservoir is therefore the sum of CGR and WGC.

320

321 During emptying,

322

323
$$\frac{P}{Z} = \frac{P_{max}}{Z_{max}}\left(1 - \frac{WGC}{WGC+CGR}\right) \qquad (7)$$

324

325 During injection,

326

327
$$\frac{P}{Z} = \frac{P_{min}}{Z_{min}}\left(1 + \frac{WGC}{CGR}\right) \qquad (8)$$

328

329 Finally, the emptying time period (t_e, in days) is the time necessary to empty the whole WGC

330 at the rated deliverability D_R, which is the design flowrate for the reservoir and all its wells.

331

332
$$t_e = \frac{WGC}{D_R} \qquad (9)$$

333

334

335 D_R is the sum of the individual deliverability D_w for each well associated with the reservoir.

336

337 Although t_e is not a time period that can be observed in practice (as deliverability fluctuates with demand), it is a useful

338 concept to define the type of storage scheme. In natural gas storage, emptying periods longer than 80 days define base

339 load or seasonal storage facilities whereas periods of less than 30 days are common for peaking-load facilities [31].

340

341 The deliverability equation used in this study, proposed by [32], has a theoretical basis and describes the gas flow rate of a well

342 in terms of the pressures involved and two parameters, *a* and *b*:

343

344
$$P_{si}^2 - P_f^2 = aD_w + bD_w^2 \qquad (10)$$

345

346 in which:

347 D_w = well deliverability at pressures P_{si} and P_f , in MMm^3/day

348 P_{si} = shut-in pressure measured at surface, in MPa[a]. P_{si} was identified with P_{max} in equations (7) and (8).

349 P_f = flowing pressure measured at surface, in MPa[b]

350 a = coefficient related to the Darcy flow in the reservoir, in MPa^2/(MMm^3/day)

---

[a] The shut-in pressure P_{si} is measured at surface after the well has been shut and allowed the appropriate time for stabilisation. P_{si} is representative of the average reservoir pressure, corrected for the hydrostatic fluid column in the wellbore.
[b] The flowing pressure P_f is also measured at the surface level but with the well flowing under stabilised conditions.

351   b = coefficient related to the non-Darcy flow in the reservoir, in MPa^2/(MMm^3/day)^2

352

353   This equation can also be used during injection provided that the sign of one of its side is changed.

354

355   The coefficient a is related to fluid properties and reservoir and well conditions through:

356

357
$$a = 1.2927 \cdot 10^6 \frac{\mu ZT}{kH}\left[1.151 log\left(\frac{10.06 A_w}{C_A A_w^2}\right) - \frac{3}{4} + s\right] \qquad (11)$$

358

359   with:

360   μ = gas viscosity at reservoir conditions, in Pa $\cdot$ s

361   T = reservoir temperature, in K

362   Z = compressibility factor at reservoir conditions (P; T)

363   k = gas permeability, in mD

364   H = reservoir thickness, in m

365   A_w = well drainage area, in m^2

366   C_A = drainage area shape factor, related to grid pattern and locations of wells within it [33]

367   r_w = wellbore radius, in m, assumed 0.1143m (large bore common in storage scheme)

368   s = skin factor, related to formation damage

369

370   The coefficient b in equation (10) accounts for the non-Darcy effects of the pore space near the wellbore wall and is related to

371   fluid and reservoir properties through:

372

373
$$b = F\mu Z \qquad (12)$$

374

375   with:

376   F = non-Darcy flow coefficient, in MPa^2/[Pa·s(MMm^3/day)^2],

377

378   The non-Darcy flow coefficient F depends on the fluid and reservoir conditions near the wellbore wall and is directly

379   proportional to the gas relative gravity at standard conditions and inversely proportional to the gas viscosity:

380

381
$$F = c\,{}^{\gamma_g}\!/_\mu \qquad (13)$$

382   in which:

383   c = parameter that can be assumed dependent on reservoir properties only

384   γ_g = gas relative gravity at standard conditions (air=1)

385

386   In this work, we used field parameters and fitted deliverability data from the existing Rough Gas Storage Facility to equation

387   (10) so as to estimate the corresponding a and b coefficients for methane, which we denoted a_{NG} and b_{NG} respectively. These

388   values were then converted to the corresponding ones for hydrogen (a_H and b_H, resp.) to assess the deliverabilities of a similar

389   hydrogen storage scheme. From inspecting equations (11) and (12), it is apparent that this conversion is straightforward on the

390   basis of the following transformations:

391

392
$$a_H = \frac{\mu_H z_H}{\mu_{NG} z_{NG}} \cdot \frac{k_{NG}}{k_H} \cdot a_{NG} \quad (14)$$

393

394
$$b_H = \frac{\gamma_{gH} z_H}{\gamma_{gNG} z_{NG}} \cdot b_{NG} \quad (15)$$

395

396   Values for the physical properties for hydrogen and natural gas in use in equations (12) to (15) were taken from Table 1.

397   The parameter a_{NG} for natural gas was estimated adopting the following values for the reservoir variables in equation (11):

398

399     $T =$ 348K, reservoir temperature used in this study

400     $k =$ 37.5mD, conservatively estimated at 50% of the average value in the rough reservoir, from [34]

401     $A_w =$ 21.46km^2 estimated from [8, 30]

402     $H =$ 30.5m, value reported for RGSF [34]

403     $C_A =$ drainage area shape factor, 30.90 for squared grid pattern (wells in the centre) [33]

404     $r_w =$ 0.1143m for large bore, common in storage schemes [31, 35]

405     $s =$ assumed to be nil (i.e. no damage) in this study.

406

407   The table below summarizes the data and the results:

408

409   Table 2: fitted parameters for modelling the deliverability of the reservoir when natural gas is stored.

Number of wells	D, MMm^3/d	P_{si}, MPa [30]	P_f, MPa [30]	a_{NG}, MPa^2 / MMm^3.d	b_{NG}, MPa^2 / (MMm^3/d)^2
14 [26]	18.1 [26]	25.3	6.89	29.5	323
29 [26]	36.8 [26]	25.3	6.89	29.5	346
30 [3]	42.5 [3]	25.3	6.89	29.5	276

410

411

412   In the following analysis, the surface delivery pressure P_f for the storage scheme will be assumed to be between 5 and 10MPa,

413   as the current requirements for natural gas transmission in the UK are within that range [36].

414

3 Results

3.1 Chemical stability

Clay-bearing sandstone and iron oxides were found to be stable under the reservoir conditions. However, sulphur containing assemblages were not, suggesting that conversion of hydrogen to H_2S was a possibility, especially if sulphate reducing bacteria were present. Likewise, the Sabatier reaction was thermodynamically allowed.

3.2 Biological activity

In the worst case scenario as described in section 2.2, it was found that no more than 3.7% of the hydrogen could be lost to conversion to methane and biomass over the lifetime of the storage scheme, by which time all available CO_2 in the liquid and gas phases had ran out and the concentration of Ca^{2+} ions had reached equilibrium value. The dissolution of carbonate rock contributed less than 1% of this loss.

3.3 Leakage losses

Leakage losses in the model reservoir were found to represent about 0.035% of the stored hydrogen after 12 months, including 0.029% in the aquifer and 0.006% in the cap rock. Given that values for the solubility of hydrogen took account of pressure and temperature, but assumed that the water was pure, these estimates are an upper bound. It was concluded that losses from dissolution and diffusion would be less than 0.1 %.

3.4 Operation of the reservoir

The storage performance can be analysed using the relationship between the storage variables CGR, WGC, D_R and t_e. In particular, the performance of a given hydrogen storage scheme can be compared with that of natural gas.

Figure 1 shows the deliverability plotted against the working gas capacity of hydrogen relative to the total capacity TGC (i.e. TGC = CGR + WGC), with lines of corresponding flowing pressures ranging from minimum to maximum allowable for the transmission pipeline. Figure 2 shows the same results for natural gas.

445
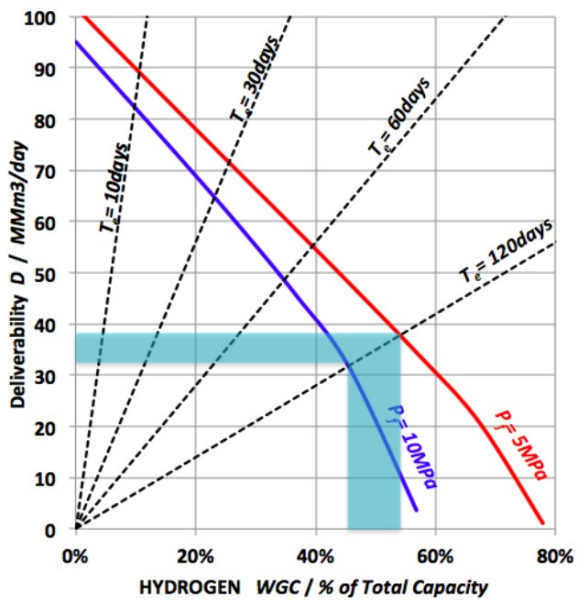
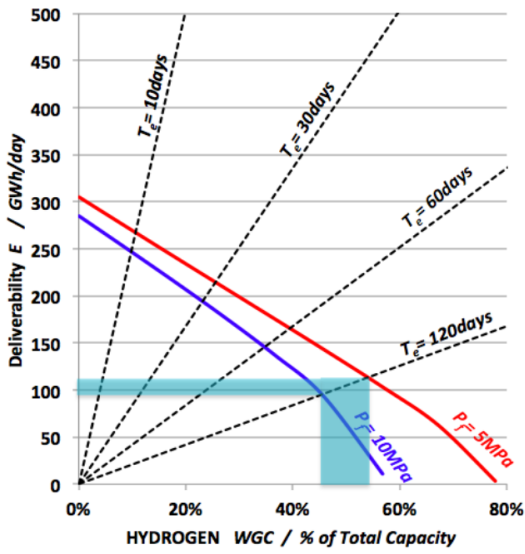446   Figure 1: Deliverability of hydrogen against working gas capacity in the model reservoir for hydrogen storage.
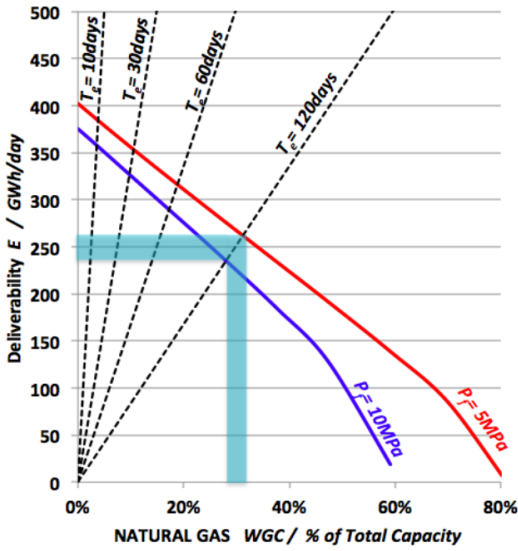
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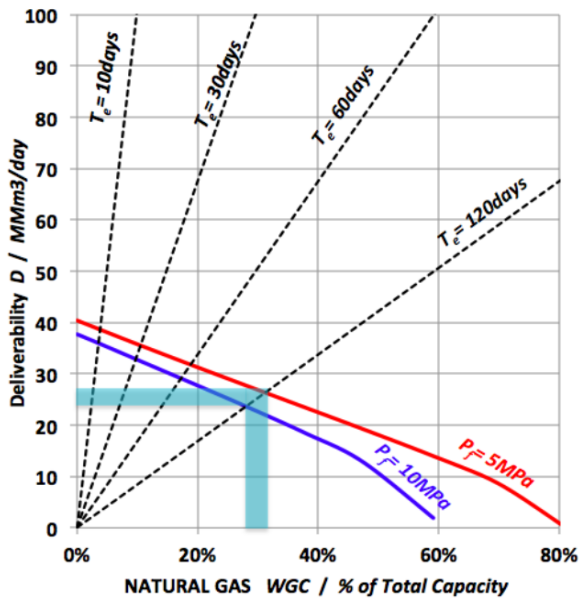
450   Figure 2: Deliverability of natural gas against working gas capacity in the model reservoir for natural gas storage.

451

452

453   Figure 3 converts the data in Figure 1 to energy flow, by multiplying the deliverability by the calorific value of hydrogen (as

454   given in Table 1). Finally, Figure 4 does the same with natural gas.

455

Figure 3: Deliverability of hydrogen in energy terms against working gas capacity in the model reservoir for hydrogen storage.

Figure 4: Deliverability of natural gas in energy terms against working gas capacity in the model reservoir for natural gas storage.

4 Discussion and conclusions

From the total storage capacity $Vs = 48$MMm^3 and by applying the equation of states for methane and also hydrogen, the total gas requirements TGC = CGR+WGC for each scheme are 8391MMm^3 of pure hydrogen and 10130MMm^3 of natural gas. The difference is due to the compressibility factors of hydrogen and natural gas at reservoir conditions (1.03 and 0.94, resp.; as reported in Table 1). Therefore, a greater compressibility factor for hydrogen has a detrimental effect on the total energy that can be stored using hydrogen instead of natural gas.

470

However, the stored volume of gas of economic interest is primarily the Working Gas Capacity, and in addition the CGR can be major component of the capital cost of any storage scheme [37, 38] if there is no segregated cushion gas already present in the reservoir which does not mix with the injected hydrogen.

Therefore, a high WGC/TGC ratio is desirable from an economic standpoint. Viable values of WGC/TGC cited in the literature, range between 0.3 and 0.7, with the high end values corresponding to salt cavern operations [9, 31, 39, 40]. As can be seen in Figures 1 and 2, a short term cycle, i.e. low t_e, is unlikely to be an economically attractive operation, given its low WGC/TGC of around 0.1. This is a consequence of the large total storage capacity of a reservoir like RGSF, in which deliverability is constrained by the number of wells available and their flow characteristics. If the number of wells were increased, then the reservoir could be emptied further, i.e. higher WGC/TGC ratio, in a shorter-term operational cycle. However, the current operation of RGSF as a seasonal natural gas storage facility [8, 30, 33] suggests that for such storage capacity, a purely short-term facility is not viable. It is important to note that this does not mean the scheme would not able to provide energy for short-term requirements but rather that it would not be economically viable on a purely short-term basis.

As highlighted in light blue in Figure 1, for a seasonal storage operation cycle of t_e = 120 days, the rated deliverability for a hydrogen storage facility, is between 30 and 40 MMm^3/day. The corresponding range of WGC/TGC is approximately between 0.45 and 0.55. Compared to the natural gas counterpart, it is interesting to note that the hydrogen scheme would work at both, greater gas deliverability and WGC/TGC ratios.

However, a better criterion for comparing natural gas and hydrogen would be a deliverability of chemical energy, that takes into account the lower heat calorific contents of 3.00GWh/MMm^3 for hydrogen (as compared with 9:94GWh/MMm^3 for natural gas), as well as the greater WGC/TGC ratio and lower TGC value. This is shown in Figures 3 and 4, where it can be seen that hydrogen can deliver 42% of the energy available through natural gas storage when considering the availability at the same surface pressure requirements. In other words, although hydrogen can store only 25.2 TWh compared to the 101 TWh stored by natural gas, hydrogen's better WGC/TGC ratio of around 0.50 compared to 0.30 for natural gas, means the hydrogen scheme can effectively store and deliver 12.6 TWh while the natural gas capability is 30.2 TWh. The latter figure matches the data published by Rough's operator [8]. Regarding deliverabilities for an emptying period of 120 days, the hydrogen storage can achieve an average of about 100 GWh/day, i.e. 40% of the 250 GWh/day for natural gas.

The losses from dissolution and diffusion of hydrogen into any underlying aquifer or overlying cap rock pores seems unlikely to cause any significant loss. The impact of dissolution in any residual oil could be checked, however in the vast majority of gas fields the underlying liquid will be water.

The presence of microorganisms and their adverse effect on hydrogen purity and losses should be considered carefully. From section 3.2, it seems that methanogenic bacteria are unlikely to contribute much loss and disruption expect perhaps in the first few cycles where a few % of the hydrogen may get consumed in extreme cases. In the case of the Sabatier reaction, the yearly losses could be reduced to less than 0.1% once biological activity was starved of carbon sources for dissolved CO_2. On the other hand, sulphate reducing bacteria could contaminate the gas with H_2S, growing on any residual hydrocarbon in the reservoir. This

suggests a requirement for careful choice of reservoirs that either had very little sulphur, or were too hot to sustain sulphate-reducing bacteria. However, the ability of micro-organisms to survive and thrive at high temperature in reservoirs should not be underestimated: hyperthermophilic, sulphate-reducing bacteria and archaea are known to accommodate temperatures in excess of 100°C [41], matching the higher range of the temperatures of existing gas fields in the Southern North Sea. In addition, many of the Southern North Sea reservoirs have gypsum or anhydrite cements, thus providing a favourable environment for these micro-organisms. While these conclusions may seem encouraging, they would require substantiation by in-situ observations and laboratory experiments, possibly on a case-by-case basis since each reservoir might have its unique lithology and microbial flora.

The degree of mixing of native and injected gases, coupled with the interaction of the gas and liquid phases should also be considered. While the experience with natural gas storage suggests a piston-like behaviour and limited mixing between injected and native gas [30], the question remains as to whether this would remain the case with hydrogen when it is injected in the reservoir.

Furthermore, the reservoirs would not be the only component of the energy system that would need to be converted from natural gas to hydrogen. Transition between the current energy economy and a 'hydrogen economy', or at least one that includes hydrogen as a significant energy vector, has been extensively studied by the NaturalHy consortium [42], suggesting scenarios where an increased proportion of the energy content of the natural gas made available in the transmission and distribution networks was contributed by hydrogen, up until the time when the mixture was replaced by pure hydrogen. The consortium was able to conclude that current gas distribution networks and appliances that conformed to existing standards would safely accommodate up to 25% hydrogen mixed within the natural gas; however uncertainty remained regarding the ability of high pressure transmission lines to prevent leakages, suggesting that upgrades may be needed in the transition to a hydrogen infrastructure.

The overall energy efficiency estimated in this study is dominated by the energy requirement of the electrolysis process. Commercially available electrolysis technology can deliver hydrogen at 30 bar with a typical conversion efficiency of around 5 kWh/Nm^3 of hydrogen, or 60% with respect to the LHV of hydrogen as has been shown in a comprehensive survey of existing installations [43], although it was mentioned in the Introduction that this figure can be improved on if lower loading of the electrolysers is considered. As a result, an average power in the order of $4 - 5$ GW would be required during a six month injection cycle to fill the reservoir to capacity, provided that cushion gas is already present.

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