

# Hydrogeochemistry of Aquifer Storage and Recovery in the Lower Greensand (London, UK) for seasonal and drought public supply

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## Abstract

Investigations are in progress to determine the potential for ASR, in the Cretaceous Lower Greensand aquifer at Horton Kirby, to meet demand during droughts of up to 2 years, whilst also meeting normal seasonal demands. The sands and sandstones are glauconitic and ferruginous so an understanding of the hydrogeochemistry is needed to predict the responses to injection of aerobic water from the overlying Chalk aquifer. Pumped and pore water from the aquifers have been characterised, microcosm experiments undertaken and the results used to constrain geochemical modelling. The transmissivity of the 23 m thick aquifer is calculated to be 45 m<sup>2</sup>/d and it contains Ca-HCO<sub>3</sub> type groundwater with a pH of 7.6 and a SEC of 329 uS/cm. Concentrations of Fe(total) and Mn exceed the prescribed concentration value (PCV). The water to be injected is also a Ca-HCO<sub>3</sub> type with a pH of 7.4 and a SEC of 537 uS/cm, is aerobic and contains elevated concentrations of nitrate (22 mg/l), but not in excess of limits. Likely impacts of ASR are reactions with Fe-minerals (including small quantities of pyrite) resulting in an increase in dissolved iron and sulphate, and removal of injected nitrate through reduction.

## Keywords

ASR, Hydrogeochemistry, Lower Greensand, UK

## INTRODUCTION

### Objectives

An ASR scheme at the Horton Kirby site in south London would be used to store potable mains water for seasonal, peak and potentially drought demand use. London and south east England rely heavily on the Cretaceous Chalk aquifer for public water supply, and the population is predicted to increase significantly in the next 20 years requiring additional supplies. The local Chalk catchment is over-abstracted and contains a sensitive low-flow river directly adjacent to the Horton Kirby site, and so to meet this additional demand Thames Water is investigating more innovative water resource management options such as ASR. A further complication is that the UK water regulator assesses Thames Water's supply capability throughout a drought period lasting 2 years. Consequently for ASR to contribute effectively to the supply capability a sufficiently large storage bubble must be maintained ready for use throughout such a drought period. Investigations are being undertaken to assess the hydraulic suitability and the likely geochemical impacts of injecting aerobic water into an anaerobic sand and sandstone aquifer containing glauconite, pyrite and other Fe-minerals. Core samples have been collected from the first investigation borehole and a second borehole is being drilled in early 2007. Flow and geochemical modelling will assist in optimising the well field configuration and recharge programme to enable seasonal use as well as allowing effective contribution to drought management.

### Hydrogeological setting

Horton Kirby is situated to the east of London, south of the Thames near the axis of the syncline forming the London Basin. The major aquifer in the basin is the Cretaceous Chalk. This overlies the Lower Greensand aquifer, which is confined and separated from the Chalk aquifer by about 70 m of Gault Clay (Table 1). The top of the Lower Greensand at the site is at a depth of 252 m below ground level and the 23 m thick aquifer is represented by the Folkestone Beds, directly overlying the Weald Clay. There is not likely to be much groundwater flow at the site as it is only 10 m AOD, the groundwater level is 6.5 m AOD.

The aquifer thickens to the south towards the outcrop at a distance of over 10 km away, resulting in a mean transmissivity of about 260 m<sup>2</sup>/d. The impact of the scheme on existing pumping stations, the nearest of which is 6.1 km away, is calculated to be less than a 1 m rise in water level given the planned injection regime. A rise in groundwater level of 0.07m is estimated at the nearest location where the river Darent flows across the Folkestone Beds, approximately 11.5 km from site.

**Table 1: Geology at the Horton Kirby borehole site**

Geological Unit	Thickness (m)	Depth to top of Formation (mbgl)
River Gravels	4	GL
Upper Chalk	41	4
Middle Chalk	71	45
Lower Chalk	65	116
Gault Clay	71	181
<b>Lower Greensand</b>	<b>23</b>	<b>252</b>
Weald Clay	N/A	275

## SAMPLING AND TESTING METHODOLOGIES

The borehole was cored throughout the entire thickness of the Lower Greensand and the core analysed as follows:

- Lithological logging
- Thin section analysis
- Whole sample mineralogical analysis by quantitative XRD (X-ray diffraction) analysis
- Clay mineralogical analysis by quantitative XRD analysis
- XRF (X-ray fluorescence) chemical analysis of whole samples
- Assessment of cation exchange capacity
- SEM and EDX analysis
- Grain size analysis
- Hydrochemical analysis of porewater samples. The samples are extracted by centrifugation, a method which is efficient in separating the fluid from the sample but does subject it to aeration. Samples are therefore handled quickly to minimise oxidation.

Four samples of core were also selected, two from Aquifer Zone 2 and one from each of Aquifer Zones 1 and 3, for batch experiments which were conducted to examine the response of adding crushed samples of the host rock into water from the potential recharge source (Horton Kirby tap water). These experiments used polyethylene bottles, mounted on a shaker housed in an incubator and kept at constant temperature, 30°C. An increase in temperature relative to the in-situ temperature (16°C) was used in order to speed up and chemical reactions taking place. Similarly, the host rock was crushed before use (size ≈ 125-250 μm) to increase the surface area for reaction. The experiments were run for approximately four weeks with sampling only at the end of the experiment. The experiments give an indication of the likely dissolution and precipitation reactions that may occur during storage of water in the aquifer.

The aquifer was also hydraulically tested with a series of step-tests followed by a 20-day continuous rate test. At the end of this period the drawdown was about 89 m induced by a pumping rate of 12 l/s. Analysis of these tests gave a transmissivity of 45 m<sup>2</sup>/d and an estimated storage coefficient of  $1 \times 10^{-4}$ . Samples were also collected during the test to characterise the groundwater in the Lower Greensand aquifer.

## RESULTS AND DISCUSSION

### Core characterisation

The mineralogical, petrographic and particle-size analysis distinguished five aquifer zones within the cored interval of the borehole (Figure 1).

*Aquifer zone 1 (253-258.5 m)* – Sediments generally poorly-sorted, medium-grained quartz-rich sandstones, with irregularly distributed detrital clay (generally smectite and illite with minor chlorite and kaolinite). A lack of Fe-bearing phases identified by XRD analysis compared with the Fe<sub>2</sub>O<sub>3</sub> content identified by XRF geochemical analysis suggests amorphous Fe-oxyhydroxides may be present.

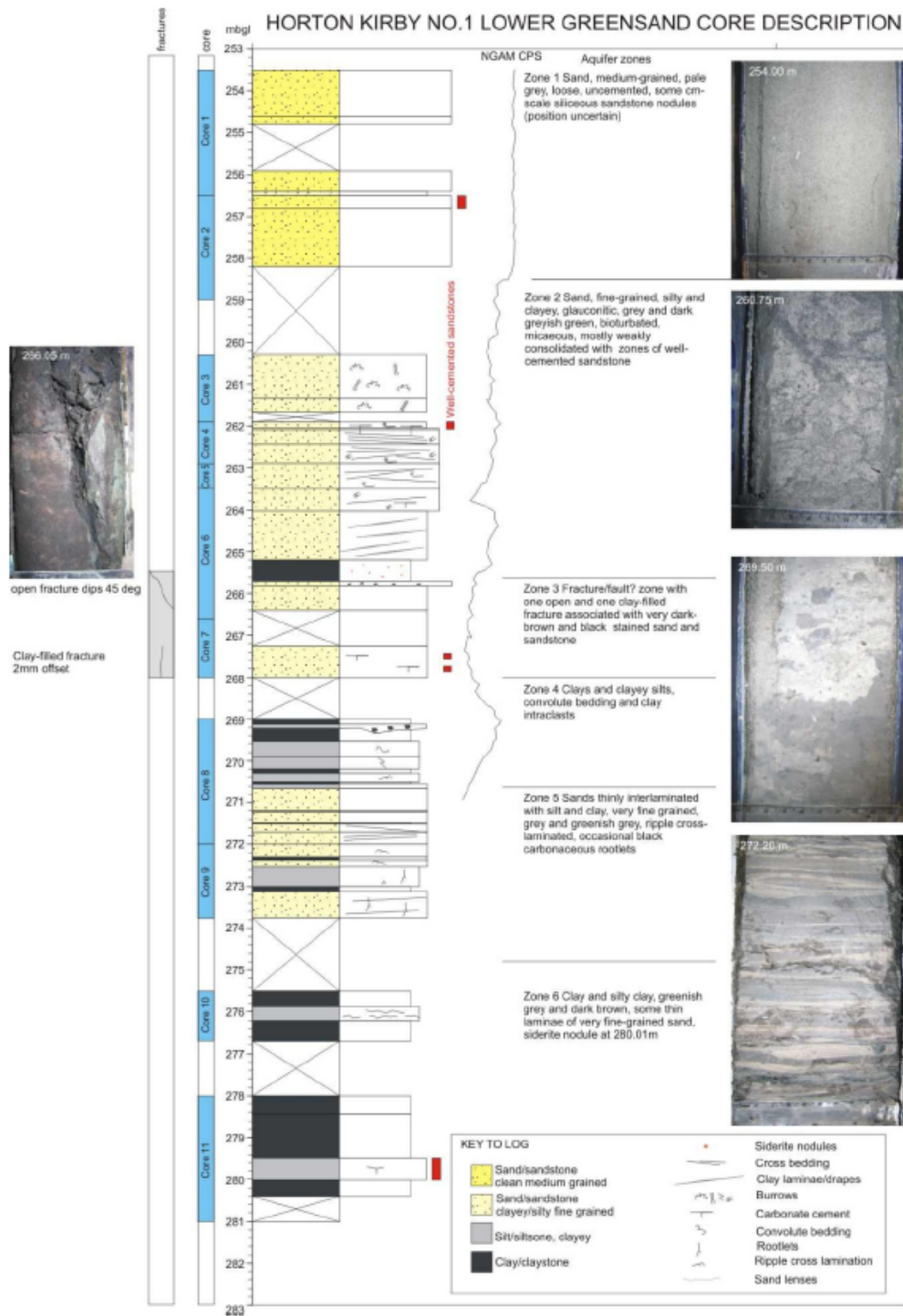
*Aquifer zone 2 (258-265.5 m)* – Upper interval (258-262 m) is similar to zone 1 but finer grained with progressively greater abundance of glauconite with depth. Again the sands have a low clay content. The zone contains some carbonate cement and traces of gypsum on surfaces, most likely to have precipitated when the samples were dried. The lower interval (262-265.5 m) comprises very poorly sorted very fine sands with abundant pellets of green glauconite. Kaolinite becomes more prominent at this depth. Carbonate cements (siderite and weakly ferroan calcite) are locally developed.

*Aquifer zone 3 (265.5-267.6 m)* – Sandstone similar to lower zone 2. However organic matter is abundant and associated with fine-grained clay, silica and authigenic Ti-oxides.

*Aquifer zones 4 & 5 (269.5-273.2 m)* – dominated by finely interbedded siltstones and mudstones. Characterised by kaolinite- and illite-dominated clay mineral assemblages with subordinate illite/smectite and chlorite.

Below aquifer zone 5 (275.4 – 280.4 m) the core largely comprises greenish grey and dark brown clay and silty clay, with some thin laminae of very fine sand.

The cation exchange capacities of two samples from Aquifer zone 2 were 39 (256.85 m) and 45 (260.48 m) meq/kg. A sample from Aquifer zone 3 (267.55 m) had a higher CEC (150 meq/kg), possibly as a result of its high glauconite content (8.5%).



**Figure 1 Geological log of the Lower Greensand core at Horton Kirby**

### Water quality analysis

The results of the analyses of the pore waters are shown in Table 2 together with analyses of groundwater pumped during the continuous rate test and water from the Chalk aquifer at Horton Kirby. These results are also plotted in Figure 2 and show the great variability in the composition of the pore water. Some of this variability may be due to contamination by the drilling and sampling process. For example, the very high pH values (up to 11.91) are likely be due to the Na-bentonite drilling fluid used when drilling the Gault Clay. A polymer fluid was then used but it was mixed with Horton Kirby water. This water has a distinctively higher Cl concentration which is seen in most of the analyses indicating that the core samples in the unconsolidated sands may also have been contaminated. However, the variability may also relate to the mineralogical and permeability variations described above.

The pumped sample is taken to represent the aquifer water as it was collected after 20 days pumping so any drilling contamination will have been well flushed out. The water will also be derived from the most permeable, and hence active parts of the aquifer, where recharge and recovery will take place. The proposed Chalk recharge water varies from the Greensand groundwater in that the former has higher SEC (537 vs. 329 uS/cm) and elevated levels of dissolved oxygen (c. 5.5 mg/l), nitrate (~22 mg/l), calcium, chloride and sulphate, and lower concentrations of iron (total and dissolved), manganese, potassium, magnesium and strontium. The pH values are similar (7.6 and 7.4).

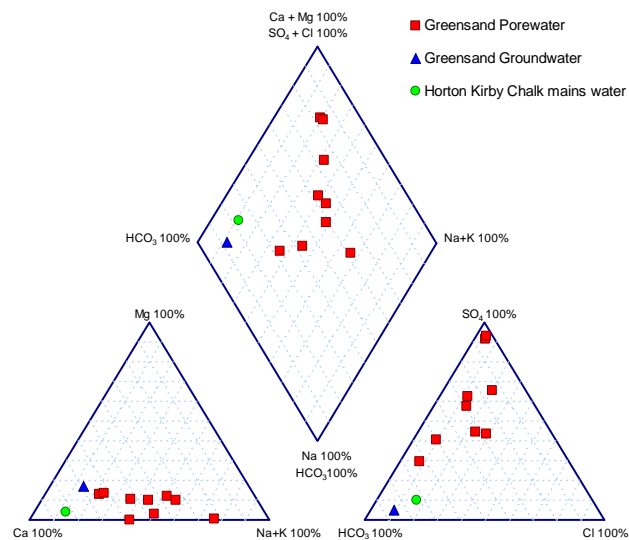


Figure 2 Trilinear plot of analyses of water from the Horton Kirby site.

### Geochemical modelling

The mineral saturation states of all the reacted fluids collected from the microcosm batch experiments were examined using the EQ3/6 (version 7.2c) geochemical modelling software package (Wolery, 1992) using the 'data0.cmp.v8.R6' thermodynamic database.

Examination of the saturation indices (SI) for the minerals shows that, in general, the fluids are not usually in equilibrium, other than with kaolinite, and are undersaturated with respect to gypsum and anhydrite. Thus if these minerals are present in the solid samples they will tend to dissolve, as suggested by the fluid chemistry results.

For the most part, the chemical and mineralogical analyses have revealed little evidence for reaction between the fluids and the solid samples. However, the sample taken to be representative of Aquifer Zone 2 (Sample MPLL720, depth 260.45-260.50 m) did react with the Horton Kirby tap water to produce an acid fluid (pH ≈ 3), and in this sample, some evidence for mineral dissolution was seen, with the removal of the previously observed gypsum/anhydrite. The presence of pyrite in the sediment could also affect the fluid chemistry.

In order to model the possible chemical reactions between recharge and native water and the Greensand aquifer material a number of scenarios have been developed using the geochemical modelling package PHREEQC, developed by Parkhurst and Appelo (1999). These scenarios were based on the equilibrium reactions of aqueous solutions interacting with minerals, gases, solid solutions, exchangers and sorption surfaces, and simulate chemical reactions and transport processes in natural or contaminated water (Appelo and Postma, 2005).

**Table 2. Porewater and pumped groundwater sample analyses from the Lower Greensand aquifer at Horton Kirby, London, UK.**

DETERMINAND	UNIT	Porewater (na = not analysed)									Pumped ASR BH	HK CHALK
		S06-00031	S06-00032	S06-00033	S06-00034	S06-00035	S06-00036	S06-00037	S06-00038	S06-00039		
		254.7 m	256.4- 256.6m	256.8- 256.9m	260.5- 260.6m	262.1- 262.2m	263.0- 263.15m	264.5- 264.6m	267.6- 267.7m	271.4- 271.5m		
PH VALUE		11.91	8.01	10.42	7.48	7.52	7.7	7.37	7.71	8.17	7.6	7.4
CONDUCTIVITY AT 20C	uS/cm	2274	1266	988	1518	488	318	1473	354	508	329	537
TEMPERATURE	deg C	na	na	na	Na	na	na	na	Na	na	16.1	na
CARBON TOTAL ORGANIC	mg/l	na	na	na	Na	na	na	na	Na	na	0.4	0.7
NITRATE AS NO3	mg/l	0.82	5.40	0.31	<0.22	<0.22	2.28	<0.22	<0.22	<0.22	<1.4	22.2
NITRITE AS NO2	mg/l	na	na	na	Na	na	na	na	Na	na	<0.01	<0.01
AMMONIUM AS NH4	mg/l	na	na	na	Na	na	na	na	Na	na	0.12	<0.05
CHLORIDE AS CL	mg/l	43.5	43.1	55.3	31.2	33.2	31.6	28	27.8	18.4	13	32
SULPHATE AS SO4	mg/l	210	311	309	810	146	64	838	70	103	8.8	26.1
ALKALINITY AS HCO3	mg/l	562	165	197	42	40	51	31	63	161	198	263
FLUORIDE	mg/l	0.256	0.267	0.597	0.258	0.402	0.396	0.261	0.361	0.374	0.06	0.1
BROMIDE	mg/l	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.048	<0.02
P (INORGANIC)	mg/l	< 0.1	< 0.1	0.18	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.071	<0.071
ALUMINIUM	mg/l	0.31	< 0.01	0.32	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.049	<0.015
BARIUM	mg/l	0.316	0.505	0.197	0.14	0.244	0.188	0.31	0.0695	0.143	0.132	0.026
BORON	mg/l	< 0.1	0.16	0.24	0.19	0.18	0.14	0.19	1.19	0.26	<0.07	na
CALCIUM	mg/l	250	161	51.9	252	49.3	28.1	234	21.9	37	50	108
IRON	mg/l	< 0.005	< 0.005	0.0115	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.79	<0.01
IRON DISSOLVED	mg/l	na	na	na	Na	na	na	na	Na	na	0.39	na
Fe2	mg/l	na	na	na	Na	na	na	na	Na	na	0.57	na
Fe3	mg/l	na	na	na	Na	na	na	na	Na	na	0.27	na
MAGNESIUM	mg/l	< 0.04	6.3	0.198	30.4	6.04	3.62	30.6	3.92	7.27	7.5	2.5
MANGANESE	mg/l	< 0.002	0.0107	< 0.002	0.0926	0.0067	0.0047	0.0402	0.0293	0.0243	0.052	<0.003
SILICON	mg/l	2.94	3.39	7.95	1.46	0.968	0.873	1.07	2.03	3.91	5.70	5.05
SODIUM	mg/l	188	186	191	83.6	31.8	25.5	76	37.5	53	9.1	16.4
POTASSIUM	mg/l	33.6	26.2	14	29.4	14	10.3	51.2	6.61	11.8	4.2	1.4
STRONTIUM	mg/l	3.73	2.8	0.608	5.33	1.25	0.714	6.54	0.715	1.38	1.22	0.26

*MixModel 1:* A simple bucket model simulating the mixing of Horton Kirby Chalk water with Lower Greensand water. The resultant solution is allowed to reach thermodynamic equilibrium with respect to  $\text{Fe}(\text{OH})_3$ , calcite and dolomite (i.e. if any these minerals are supersaturated within the solution they are allowed to precipitate). The results show that virtually all the dissolved iron in the Greensand water is oxidised and precipitates as Fe-hydroxide ( $\text{Fe}(\text{OH})_3$ ), and that calcite will precipitate from the supersaturated recharge water.

*MixModel 2:* Pyrite and calcite are added to MixModel 1, thereby simulating reaction between these aquifer minerals, recharge water and native water. The model assumes that the aquifer comprises 0.1% pyrite. The results indicate that the injection water will oxidise pyrite resulting in an increase in the concentration of sulphate and dissolved iron and a reduction in pH within the recharge water. The pyrite will be oxidised both by dissolved oxygen and nitrate within the recharge water. It is unlikely that  $\text{NO}_3$  will oxidise pyrite directly by chemical means and such denitrification has yet to be demonstrated in the laboratory (Kinniburgh et al, 1993). It is more likely that the reaction will proceed as a result of bacterially-mediated denitrification.

*MixModel 3:* The Fe stability diagram predicts that at pH (7.3-7.6) and Eh (-0.16 to -0.20V) of the solutions generated by MixModel 2, siderite ( $\text{FeCO}_3$ ) would be the solubility control of Fe. MixModel 3 therefore adds siderite to the phase assemblage, allowing it to precipitate. The results indicate that under thermodynamic equilibrium siderite will precipitate resulting in lower dissolved Fe concentrations than in MixModel 2. In the example outlined above, 22.5 mg of pyrite dissolves generating 17.5 mg of siderite (precipitate) and 1.9 mg/l dissolved Fe.

*MixModel 4:* This model develops MixModel 3 with the addition of other minerals to the phase assemblage. These minerals, noted in the XRD and thin section analyses, include: K-feldspar, gibbsite, chalcedony and chlorite 14A (closest approximation to glauconite). The model predicts that at thermodynamic equilibrium, there will be an increase in K and Mg (reaction with K-feldspar and chlorite) and a decrease in Fe (siderite precipitation), Ca and alkalinity as  $\text{HCO}_3$  (precipitation of calcite). These clay mineral reactions are likely to be slow and may take many years to reach thermodynamic equilibrium. However the simulations indicate the expected direction of change.

*ATM(atmosphere)Model 1:* This model develops MixModel 3 by allowing  $\text{CO}_2$  degassing thereby simulating the abstraction of recharge water from the Greensand aquifer. The results indicate that as degassing occurs, under thermodynamic equilibrium, calcite is precipitated resulting in a decrease in Ca and  $\text{HCO}_3$  in solution, and an increase in pH.

*ATMModel 2:* Again this model develops MixModel 3 by allowing  $\text{CO}_2$  degassing, but additionally allows equilibrium with oxygen at atmospheric concentrations, thereby simulating the abstraction of recharge water from the Greensand aquifer and subsequent exposure to air. As with ATMModel 1  $\text{CO}_2$  degassing generates calcite precipitation with the associated decrease in dissolved Ca and  $\text{HCO}_3$  and increase in pH. Reaction with oxygen results in the oxidation of dissolved ferrous Fe to Fe-oxyhydroxide, which precipitates out of solution.

All the models discussed above assume thermodynamic equilibrium between the various phases and do not take into account reaction rates. It is unlikely that, over the period between recharge and recovery, the reactions simulated in the models outlined above will go to completion. It is possible to model kinetics within PHREEQC. However this requires the user to define rate expressions which are poorly understood for the required reactions. Additionally the models do not take into account that iron precipitate (Fe-oxyhydroxide and siderite), formed as a result of reaction between pyrite and recharge water, may coat pyrite grains thereby restricting further reaction (Nicholson et al., 1990). The models are therefore likely to over-predict the amount of pyrite that will be oxidised through reaction with chalk injection water.

In addition to redox reactions, ion exchange is likely to have an impact on the quality of recharge water. Calcium concentrations in the recharge water exceed those in the native water; as a result it is likely that ion exchange will take place between dissolved Ca and Na in Na-rich clays. This ion exchange would result in an increase in dissolved Na and a decrease in dissolved Ca.

## CONCLUSIONS

The main mineral of concern within the Greensand aquifer is pyrite ( $\text{FeS}_2$ ), oxidation of which would result in the generation of dissolved ferrous iron ( $\text{Fe}^{2+}$ ) and sulphate. The ferrous iron may then be further oxidised and precipitate out of solution as iron-oxyhydroxide ( $\text{Fe}(\text{OH})_3$ ) or, depending on the Eh and pH of the recharge water, as siderite ( $\text{FeCO}_3$ ), possibly causing some clogging of the aquifer. Acidity produced by pyrite oxidation may react with auxiliary minerals in the Greensand such as glauconite and other micaceous minerals, Na and K feldspar and calcite, resulting in an increase in concentrations of Mg, Ca, K and Na.

Further investigations at the Horton Kirby site, including the implications for long-term bubble storage for drought use, will be guided by the results to date. Improved understanding of the injection water -aquifer- native water interactions will be gained through monitoring key determinands, including:

*Cl:* Since the Cl concentration of native LGS groundwater (13 mg/l) is lower than the concentration in the potential injection water (~30 mg/l), the Cl concentration of the abstracted water will provide an indication of recovery efficiency.

*Fe (total and dissolved):* Concentrations will give an indication as to the degree of interaction of injection water with Fe-minerals within the Greensand (and interaction with dissolved Fe within native groundwater).

$SO_4$ , Mg, Ca, Mn, Sr, Na, K and  $HCO_3$  (alkalinity) – Concentrations will give an indication of the degree of interaction of injection water with aquifer minerals and native water.

*N-species*: Nitrate in the injection water is likely to be reduced so measurements of  $NO_3$ ,  $NO_2$  and  $NH_4$  will therefore be useful in identifying the degree of reduction within the LGS.

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