BRITISH GEOLOGICAL SURVEY
Natural Environment Research Council

COMMISIONED REPORT CR/01/54
Groundwater Systems and Water Quality Programme

Aquifer Storage and Recovery

Physical and Geochemical Modelling (SWIFT-PHREEQC) of British Aquifers for Aquifer Storage and Recovery Purposes

Part 2: Geochemical Modelling

I Gaus

This report was prepared as a contribution to ASR-UK; a project funded by a Foresight LINK award and a UKWIR Ltd research contract

Bibliographic Reference

Gaus I, 2001
Physical and geochemical modelling (SWIFT-PHREEQC) of British Aquifers for Aquifer Storage and Recovery Purposes.
Part 2: Geochemical Modelling
British Geological Survey Report CR/01/54

British Geological Survey Keyworth, Nottinghamshire

Contents

List of Figures

(All figures are at the end of the report text)

List of Tables

EXECUTIVE SUMMARY

This report describes the progress that has been made in developing models simulating both the physical and geochemical aspects of Aquifer Storage Recovery (ASR) schemes. This work is part of a 30 month project, entitled ASR-UK, which started in April 1999. This report follows on from the work reported in Gaus et al., BGS report WD/00/08, published in March 2000.

The aim of this report is to explore and to assess the chemical limitations or benefits in applying ASR in the major UK aquifers: the Chalk, the Lower Greensand, the Triassic Sandstone and the Jurassic Limestone.

The implications for the quality of the recovered water using different types of injection water and different types of native water are assessed using two types of modelling: mixing modelling and cycle modelling. A total of 13 different combinations were developed. An example of more detailed geochemical modelling based on observations from an ASR-site in the Chalk is also included. More complex modelling requires detailed knowledge, particularly on the solid phases in the aquifer, but such data are generally limited.

To assess the likely chemical quality of the recovered water when planning an ASR-scheme three components have to be taken into account:

- chemical aspects of the injected water;
- chemical aspects of the native water in the aquifer;
- geochemistry of the aquifer and the chemical interaction with the injected water (e.g. dissolution of pyrite).

Major chemical changes to the quality of the injected water during recovery are expected when one or more of the following conditions are met:

- there is a large difference in chemical condition between the injected and the native water; this can cause large differences in pH or redox condition.
- the native water or the sediment do not possess a sufficient pH buffering capacity (e.g. in the case of acidic waters where no calcite is present for dissolution)
- there is a large difference in elemental concentrations between the injection and the native water (e.g. fluoride) and significant mixing occurs (e.g. in dual porosity aquifers)
- a change in chemical condition of the water having contact with the sediment is able to trigger major (e.g. dissolution of gypsum) or minor (e.g. dissolution of heavy metals) reactions.

The conclusions are based on the modelled cases only, and highlight the main chemical reactions likely to occur when implementing an ASR-scheme. Other chemical interactions may determine the quality of the recovered water when other injection waters are used, the native water has a different quality, or the geochemistry of the aquifer is different from the one assumed here. Also minor reactions and elemental concentrations are in general not modelled.

Within this study it was also clearly illustrated that the geochemical model can be used at different levels when planning an ASR-scheme. At the initial desk-study level, geochemical modelling can be used as a crude assessment of the chemical viability of the scheme. In subsequent stages of the ASR-scheme trial and implementation, geochemical modelling can be supported by the observed data, used to assess the impact of specific geochemical reactions as illustrated for fluoride in the ASR-trial in the Chalk.

1. INTRODUCTION

The aim of this report is to explore and to assess the chemical limitations or benefits in applying ASR in major UK aquifers: the Chalk, the Lower Greensand, the Triassic Sandstone and the Jurassic Limestone. This report therefore links up with the previous report by Gaus et al. (2000) entitled: "Physical and Geochemical Modelling (SWIFT-PHREEQC) of British aquifers for ASR-purposes. Part 1: physical modelling and geochemical model calibration". In this report the geochemical modelling is more fully developed.

The implications for the chemical quality of the recovered water using different types of injection water and different types of native water are assessed using two types of modelling: mixing modelling and cycle modelling. A total of 13 different combinations were developed. An example of more detailed geochemical modelling based on observations from an ASR-site in the Chalk is also included. More complex modelling requires detailed knowledge, particularly on the solid phases in the aquifer, but such data are generally limited.

All injection and native water types as well as the geochemistry for the different aquifers, which were used for the modelling, are assumed to be representative. However, in reality, due to large spatial variations this cannot be the case. The conclusions of this report are therefore meant as an initial assessment on what the likely chemical problems or benefits might be in implementing an ASR scheme in a UK-aquifer. The conclusions drawn are therefore generic in that typical analysis for injected water, groundwater and rock geochemistry are used. However, the models should be tailored with actual measured data when site specific investigations are being undertaken.

2. LIMITATIONS OF PHREEQC FOR ASR-DUAL POROSITY MODELLING

The applicability of PHREEQC for modelling geochemical changes during ASR-schemes was described by Gaus et al. (2000) and is further developed here. The calibration of the modelling results of PHREEQC to the results of SWIFT was executed by adapting the exchange factor (controlling diffusion between matrix and fractures) in PHREEQC until an optimal fit between both model results was obtained. The optimal calibration was achieved and tested for one example (1 ASR-time-scheme based on 2 ASR-cycles of 1 year each).

However, when using PHREEQC for geochemical modelling of ASR-schemes one should test how robust this calibration is. The simplified dual porosity approach in PHREEQC might render the calibration parameter (the exchange factor) time dependent and this might limit the use of PHREEQC for longer ASR schemes. The conditions of the time and space discritisation because of the one-dimensionality of PHREEQC, might lead to the fact that PHREEQC is inappropriate for short ASR-cycles (which are often used during testing). Therefore three further examples were tested:

short term testing:	4 ASR-cycles of 4 months each
long term testing:	8 ASR-cycles of 1 year each
	2 ASR-cycles of 5 years each

The physical parameters for the cycle testing are described in detail in Gaus et al. (2000).

Further tests indicate (Fig. 1) that the results for PHREEQC match with the results of SWIFT for long timescales (up to 10 years). This is the case for both a large number (eight) of short cycles (1 year) and a small number (two) of very long cycles (5 year). The modelled concentrations during the standing periods after recovery are slightly lower for PHREEQC than for SWIFT, but these differences stay within an acceptable range. For ASR-cycles shorter than the calibration example, the modelled PHREEQC concentrations start to differ more. PHREEQC produced higher concentrations during the standing phase after the injection and the recovery phase, and lower concentrations during the standing phase after the recovery and the injection phases. Further testing on shorter cycles showed an even larger deviation. This might be caused by the time dependence of the exchange factor or by concentration changes close to the well (where PHREEQC cell lengths are large) which become more important in short cycle time-schemes than in long cycle time-schemes. Further testing is necessary to determine the exact cause of this deviation.

It is therefore concluded that, based on these results, PHREEQC can be used to model geochemical aspects of ASR (taking into account (radial) transport and dual porosity) in the case of operational cycles (long time-schemes) but is less effective at present when modelling test cycles (short time-schemes).

3. GEOCHEMICAL MODELLING

3.1 Introduction

The geochemical processes involved in an ASR scheme comprise a range of chemical reactions between the injection waters, the native groundwater and the aquifer. The chemical changes that occur are determined by three end-members:

- chemical composition of the injected water;
- chemical composition of the native groundwater;
- chemical (mineralogical) characteristics of the aquifer.

There are large potential variations in the chemical composition of both the injection and the native waters. The source of the injected water can vary considerably including drinking water, untreated or treated surface water, untreated or treated groundwater or reclaimed water. Native groundwater quality can vary from fresh through brackish water to saline water. It can be dominated by equilibrium involving carbonate or silicate mineral phases and the prevailing conditions in confined aquifers may be oxidising or reducing. It can usually be assumed that the native groundwater is in equilibrium with the host rock, although this is not always the case. In addition, large regional differences exist in native groundwater quality related to residence time and differences in aquifer mineralogy.

In this chapter geochemical modelling of ASR was carried out on the four main aquifers in the UK: the Chalk, the Lower Greensand, the Sherwood Sandstone and the Jurassic Limestone.

For each of the aquifers, modelling was undertaken using different injection waters to assess the possible quality changes this might have on the recovered water. The objective of this modelling exercise was therefore to provide guidance on water quality issues when planning new ASR-schemes. However, where an ASR scheme is to be implemented, more detailed modelling based on site specific data will be necessary to assess potential water quality changes in the recovered water.

The main geochemical processes relevant to ASR include mixing, adsorption-desorption, ion-exchange, oxidation-reduction and dissolution-precipitation reactions and were described earlier (Jones et al., 1999).

3.2 Modelling Approach

For each aquifer, different injection and native groundwater types were selected and modelled. A geochemical conceptualisation was initially developed involving different modelling scenarios defined by different geochemical processes. These modelling scenarios produced a range of potential recovered water qualities rather than a single outcome and are likely to represent the range of water qualities expected from ASR operations in a single aquifer.

3.2.1 Water quality selection

Groundwater quality generally varies significantly within the same aquifer both areally and with depth. Therefore, a selection of native groundwater types was used for modelling purposes. For the same reason injection waters were selected from the broad range of potential injection waters for each aquifer. The final selection was based on:

- the availability of a complete and reliable chemical analysis;

- the likelihood of the water-type being used for an ASR-scheme;
- the extent to which the native water-type represents the typical hydrochemistry in the part of the aquifer showing potential for ASR development.

Although summaries of chemical data exist for different aquifers, individual analysis were used in the model.

Reasons for this are:

- statistical measures (mean, median) of chemical data of water samples do not represent real analysis (e.g. the mean concentration of chemical parameters in a dataset might not represent any groundwater present in the aquifer);
- ionic balances of statistical measures are meaningless;
- the chemical composition of a single water analysis is controlled by the underlying geochemical processes; this is not the case for a collection of statistical measures.

However, where surface waters were used as injection waters some summary data were used because surface waters are most likely to be influenced by mixing and are not likely to characterise ongoing processes.

3.2.2 Conceptual modelling

A selection of the most important and most relevant processes for ASR-purposes was made and included in the geochemical models. The conclusions are based on these processes only.

It is impossible to include all potential geochemical processes in an aquifer. Chemistry data are often not detailed enough and the geochemistry of the aquifer is seldom sufficiently understood. The influence of many minor minerals and trace element species were not modelled. For information concerning minor elements (e.g. heavy metals) and accessory minerals, accurate data concerning the aquifer mineralogy at the sampling sites as well as more complex modelling is necessary. However, if the injection or native water contains significant concentrations of minor elements (e.g. fluoride), their likely influence on recovered water quality is discussed.

Geochemical modelling was carried out under the assumption that chemical equilibrium is established between the injection water, the native water and the aquifer material. Modelled concentrations are therefore likely to overestimate the impact of a geochemical reaction. In many cases chemical equilibrium is not achieved because of sluggish reaction kinetics with respect to the ASR-timescale, limited presence of the mineral in the aquifer or limited availability of the mineral for dissolution.

Taking into account reaction kinetics would allow for more accurate modelling but would also complicate the modelling considerably because:

- accurate reaction kinetics of many processes are not known, the parameters which describe these processes are not known and/or are very site specific;
- no full chemical analysis at the site is available;
- the availability of the minerals is unknown (e.g. even if pyrite is available in the sediment the mineral surface might be covered with iron-oxides or the mineral might be embedded in clays and will therefore not take part in any reaction);

- kinetic reactions are dependant on the specific surface areas of the minerals present which requires detailed study.

To obtain a more complete insight into how the recovered water quality could be affected, the geochemical model PHREEQC was used in two modes:

- Mixing of the native water and the injection water taking into account potential geochemical reactions with the aquifer minerals;

- ASR-cycle modelling also taking into account potential geochemical reactions with the aquifer minerals. This modelling is based on a hypothetical ASR-scheme and takes into account the physical condition and flow mechanisms of the aquifer (e.g. single or dual porosity aquifer). The ASR-cycle modelling with PHREEQC is described in detail in Gaus et al. (2000).

Although the different models provided elemental concentrations, the main conclusions are semi-quantitative because of the restrictions of the conceptual modelling. General guidelines on the direction in which the recovered water quality might evolve are discussed.

3.2.3 Aquifer modelling

For each aquifer a short discussion on the main hydrogeochemical processes is included, the model conceptualisation is discussed, and the modelling results are interpreted.

3.3 The Chalk

3.3.1 General

The Chalk aquifer is generally most productive in the top 50 m below groundwater level or the top 50 m below a confining layer (Jones et al., 1998). At greater depths, residence times of the water increase due to the very slow groundwater flow or, at greater depths, effective absence of groundwater flow. Larger residence times generally lead to more mineralised groundwaters and therefore a poorer native water quality.

For the modelling of simple mixing the dual porosity character of the Chalk has not been taken into account. The dual porosity nature of the Chalk has two major implications:

- During ASR the native water in the fractures will be replaced quickly with injected water. However, diffusional interchange between the matrix and fractures is relatively slow with the matrix retaining the native water signature for a long time. This diffusional mixing might lead to additional important geochemical reactions.

- The water quality within the pores of the matrix of the Chalk may differ significantly from the water residing in the fractures (Shand, 1999). Such differences may have important implications for the recovered water quality in an ASR scheme.

The effect of dual porosity on the resulting quality of the recovered water is assessed using the cycle modelling.

3.3.2 Hydrogeochemical processes in the Chalk

An overview of the hydrogeochemical processes in the Chalk is given in Edmunds et al. (1989):

1. Oxygen concentrations are reduced to zero over a residence period of about 25 or more years.

Reducing conditions allow Fe^{2+} concentrations to increase and, beyond the redox boundary, NO_3 is rapidly reduced following the removal of oxygen. Sulphate concentrations increase and reduction of sulphate to sulphide is only a very minor process.

2. Along the flow path, there is a progressive increase in Mg and Sr and more positive $\delta^{13}C$ values indicating that progressive dissolution of carbonate is taking place, probably by incongruent solution.

3. Several cations (e.g. K, NH_4, Li) increase in concentration along the flow gradient as a result of ion exchange between the younger lower salinity groundwaters and 'marine' clay minerals.

4. Cation-exchange reactions are relatively unimportant for Na and this generally amounts to a maximum equivalent of 30 mg l^{-1} Na. However, in parts of the Wessex basin this can be significant (Buckley et al., 1998)

5. Salinity is greatest in the deepest groundwaters. This can be related to the underlying interstitial waters which have even higher salinities resulting from residual connate water.

6. Reaction with the Chalk rock is likely to release Mn, Sr and possibly other trace metals in small quantities in proportion to the Ca and Mg dissolved.

Where the Chalk aquifer is under reducing conditions, the presence of pyrite is possible as reported in Morgan-Jones (1977) and Shand (1999). In the non-carbonate fraction of the Chalk, clays are the most important minerals. Morgan-Jones (1977) reports mica and montmorillonite being present throughout the Chalk, particularly in the Lower Chalk.

Trace elements in the Chalk native groundwater, which commonly exceed drinking water standards, seem to be restricted to Fe, Mn and F (Edmunds et al., 1989).

3.3.3 Conceptualisation of the hydrogeochemistry of the Chalk

Mixing modelling.

Two scenarios were modelled for each combination of the selected native and injection waters.

In scenario 1 simple mixing was modelled. This implies that only chemical reactions as a consequence of the mixing of two water samples were modelled. In the model, chemical equilibrium was re-established. The type and impact of these chemical reactions depend on the composition of the mixture and the degree to which individual parameters behave in a conservative manner. Scenario 1 does not take into account any interaction with the minerals forming the aquifer.

In scenario 2 mixing was modelled taking into account interaction with the aquifer minerals. The interaction of the groundwater with the aquifer was based on the geochemical description given earlier. The following processes were included:

- saturation with calcite
- saturation with dolomite
- saturation with montmorillonite
- saturation with pyrite
- saturation with siderite (might precipitate when pyrite dissolves in large amounts)

The saturation with respect to a certain mineral implies that this mineral is available in the aquifer and will dissolve until the saturation index is reached. This assumption is likely to be realistic in the case of calcite, which is abundantly available in the sediment and for which the dissolution kinetics is fast. However, dissolution of pyrite is often kinetically hindered (Appelo and Postma, 1993) and might not be directly available for dissolution. Although some pyrite might dissolve it is highly unlikely that pyrite will reach saturation in the recovered water.

Cycle modelling.

The ASR cycle was modelled as a 1-year cycle with an injection rate and recovery rate of 45 m^3/d per fracture. The injection period lasted for 4.1 months, the water was allowed to remain in the aquifer for 2.6 months after which a recovery period of 2.6 months followed by another standing period for 2.6 months was modelled. The dispersivity and the diffusion coefficient were set at 10 m and 10^{-9} m^2s^{-1} respectively. This is a rough estimate, since more accurate estimates are not directly available. Since the input parameters are hypothetical, the modelled concentrations only indicate general trends in quality during ASR.

The porosity of the fractures is assumed to be 1% and the matrix porosity 30%. The value of the exchange coefficient was calibrated to 5 x 10^{-8} s^{-1} (Gaus *et al.*, 2000).

Chemical reactions taken into account were those resulting from simple mixing as a consequence of the injection of Chalk groundwater in the Chalk aquifer at Lytchett Minster.

3.3.4 Selected water types

The hydrochemical data for all the water types are listed in Table 1; the location of the native waters within their aquifers is shown in Fig. 2. A Piper diagram of all the samples is shown in Fig. 3.

Native water.

Two native water types were chosen. Both samples were taken from exploration sites in Wessex: one from the Lytchett Minster borehole and one from the Holton Heath borehole. Both types represent a typical composition of a confined Upper Chalk groundwater.

Both samples are at saturation with respect to calcite and quartz, the Lytchett Minster sample is also at saturation with dolomite. No oxygen or nitrate is present and the redox measurements show that the waters are slightly reducing. They are also at saturation with respect to fluorite. The main difference between the samples lies in the higher salinity of the Holton Heath sample.

Injection water.

Jones at al. (1998) identified two potential water types that could be used as injection waters in the Chalk: groundwater from the Chalk aquifer itself and surface water collected in a small reservoir and subsequently treated.

Two different examples of injection water were therefore included in the modelling exercise: treated Chalk groundwater and treated surface water (from Blashford Lakes).

The Chalk injection water is oxidised and saturated with respect to calcite and quartz, and is less mineralised than both native groundwaters. Nitrate concentrations are relatively high at 16 mg/l. The Blashford Lakes treated surface water is assumed to be at saturation with oxygen and is relatively high in sulphate (117 mg/l), whereas nitrate concentration is low. Both injection waters also have low fluoride concentrations.

3.3.5 Results

Mixing modelling.

In Table 2 the effects of using different injection and native water types on the resulting recovered water quality is shown. Injection of both the Chalk injection water and the Blashford Lakes treated surface water in the Chalk at Lytchett Minster and at Holton Heath were modelled. The modelling results for the two native water types were not significantly different the results for both cases are therefore discussed together.

In Fig. 4, the evolution of pH and the dissolved iron concentration are illustrated for each of the 4 cases. Each graph represents the evolution of a chemical parameter along a mixing line going from 100 % native water (left) to 100% injection water (right). The simple mixing line and the mixing + equilibrium line indicate a range within which the real concentration would be situated.

Example of cycle modelling.

Results of the cycle modelling are shown in Fig. 5. Three of the four parameters (pH, Fe, SO_4) shown are influenced by the chemical interactions. This is not the case for fluoride which is modelled to behave conservatively. Two injection-recovery cycles are shown. Each injection-recovery cycle consists of four parts corresponding to the sequential injection-stand-recovery- stand phases.

The fact that the Chalk aquifer behaves as a dual porosity aquifer means that differences in elemental concentrations between native and injection waters lead to large variations in water quality at the well during the different phases of an ASR-cycle.

Table 1 Hydrochemical data used for the Chalk modelling

		NATIVE GROUNDWATER		INJECTION WATERS	
		Chalk Holton Heath	**Chalk Lytchett Minster**	**Chalk groundwater**	**Blashford Lakes Water**
			Wessex Water	Wessex water	Wessex Water
		XY: 406 107	XY: 396 093		
Parameter	**Units**				
Temperature	C	13	13	10.5	18
pH		7.3	7.6	7.31	6.7
Dissolved Oxygen	mg/l	0	0	11.2	11.3*
E_h	mV	-16		693	
Bicarbonate	mg/l	302			
Alkalinity	mg CaCO3/ l		246	185	41
Potassium	mg/l	4.7	4	3.1	2.5
Sodium	mg/l	117	46	15.2	28
Calcium	mg/l	50.5	63	110	48
Magnesium	mg/l	16.4	20	4.4	3.4
Iron	mg/l	0.439	1.4	0.04	0.02
Sulphate	mg/l	21.8	34	21	117
Nitrate	mg N/l	0.001	0.15	5.64	0.61
Nitrite	mg N/l	0.001	0.003	0.01	n.d.
Ammoniacal N	mg N/l	0.19	0.21	0.01	0.02
Chloride	mg/l	119	58	29	29
Fluoride	mg/l	3.9	3.35	0.18	n.d.
Silica	mg/l	8.06	12.4	5.5	0.8
Dominant redox couple to calculate E_h		none	N(5)/N(3)	none	O(-2)/O(0)
Mass balance		-3.72	3.87	10.56	-2.12
Saturation indices					
Calcite		-0.23	0.21	0.02	-1.48
Dolomite		-0.78	0.08	-1.23	-3.86
Quartz		0.28	0.46	0.16	-0.81
Fluorite		0.16	0.13	-2.09	n.a.

* assumed at saturation

Table 2 Overview of the impacts of ASR in the Chalk using the selected water types

	Injection Waters	
Native Groundwater	GROUNDWATER EXAMPLE Chalk injection water Lytchett Minster	SURFACE WATER EXAMPLE Blashford Lakes treated surface water
Chalk Lytchett Minster & Chalk Holton Heath	*General issues* • High fluoride concentrations in the native water might result in elevated concentrations because the recovered water might contain a significant component of the native water. • In more evolved Chalk waters (as is the Holton Heath native water), Na concentrations in the recovered water might become significant. • High iron concentrations in the native water are likely to decrease when mixing with the injection water because of oxidation of dissolved iron and precipitation as iron oxides.	
	Specific issues • Only slight pH changes will occur (< 1.0 pH units) • Increase in Ca-concentration - The establishment of the carbonate equilibrium can induce a doubling of the Ca-concentrations in the case of pure injection water coming into contact with the sediment. • Reduction of dissolved oxygen – where pyrite is available in the aquifer a reduction of the dissolved oxygen might occur. • Increase in sulphate concentration – Dissolution of pyrite (if available) would lead to a sharp increase of the sulphate concentration in the most extreme case. • Increase in dissolved iron – Depending on the availability of pyrite an increase in dissolved iron could take place (up to several mg/l). An amount of +/- 1 mg/kg available pyrite per kg sediment could induce this increase. In the case where the dissolved iron concentration increases sharply, precipitation of siderite might occur limiting the increased concentrations. However, slow reaction kinetics and/or availability are likely to limit pyrite dissolution.	*Specific issues* • The original high sulphate concentrations in the injected water will remain since it is not involved in any reaction. • In the case of intensive mixing with the native water an increase in pH > 8 is possible. • Reduction of dissolved oxygen and nitrate - In the case where pyrite is available in the sediment a reduction of the dissolved oxygen, but secondly also of nitrate might occur. The presence of +/- 1 mg pyrite per kg sediment would reduce the nitrate present in the injection water to zero. • Increase of dissolved iron - Depending on the availability of pyrite an increase in dissolved iron can be expected. However, this increase is likely to be less than in the case of the Chalk groundwater used as injection water. In the case where dissolved iron concentration increases sharply, precipitation of siderite might occur and limit or lower the increased concentrations. However, slow reaction kinetics and/or availability are likely to limit pyrite dissolution.

3.3.6 Applications of ASR in the Chalk

ASR trial at Lytchett Minster – detailed fluoride modelling

Wessex Water plc carried out an ASR-trial in the confined Chalk at Lytchett Minster in southern England.

A total of 9 injection and recovery cycles were carried out at the trial site in order to measure the water quality changes under different injection/abstraction regimes and to start to build up a "buffer zone" between the injected and the native water. Cycles varied considerably in length of time of injection and recovery periods and rates. While the injected water was of potable quality, the native groundwater was not potable due to high concentrations of fluoride (3.6 mg l^{-1}) and iron (0.34 mg l^{-1}).

Apart from the first cycle, less water was recovered than was injected in order to build up a buffer zone. The water injected over nine cycles totalled about 980 Ml, of which 360 Ml was recovered. Using a fracture porosity of 0.01, the maximum radius of the "bubble" of injected water was calculated to be about 800 m and the residual "bubble" about 700 m.

A physical model to quantify the role of dual porosity effects in an ASR scheme was developed and calibrated (Williams et al., 2000). The SWIFT modelling showed that the dual porosity nature of the Chalk resulted in significant diffusive mixing which led rapidly to a large component of the native water in the recovered water. Due to the large volume of fluoride stored in the native groundwater within the matrix, the fluoride concentration in the recovered water will only decrease slowly during subsequent cycles.

Furthermore, it was discovered that the high fluoride concentrations could be a consequence of processes other than diffusive mixing in a dual porosity aquifer. Fluoride concentrations in the recovered water were higher than those expected from simple mixing alone and it was concluded that the additional fluoride (approximately 10%) was possibly caused by the dissolution of fluorite in the aquifer. However, the recovered water does not reach saturation with respect to fluorite.

An indication of the excess fluoride in the recovered water is shown in Fig. 6 for selected cycles (cycles 1, 7, 8 and 9). Chloride (which shows conservative behaviour) was used to calculate the amount of mixing between injection and native water and is shown on the x-axis. The ratio between mixing based on fluoride to that based on chloride is plotted on the y-axis. If fluoride also behaved conservatively, the fitted line would be horizontal (intersecting the y-axis at 1) indicating that both mixing estimates are the same. The fact that this ratio is much higher than 1 at the beginning of each recovery cycle, and reduces during the recovery phase, indicates that processes other than simple mixing determine the fluoride concentration. One can observe that where the main component of the recovered water is injection water, the fluoride content is much higher than would be expected from simple mixing. With increasing percentage of native water in the mixture, excess fluoride due to geochemical reactions will influence the fluoride mixing ratio to a lesser degree because of the high fluoride concentration present in the native groundwater. Geochemical influences on fluoride concentrations are therefore most obvious during the early part of the recovery cycle, in mixtures dominated by injection water.

The PHREEQC model was used to model the fluoride concentrations in detail. Physical parameters used and details of the modelled ASR-cycles are shown in Table 3.

Mineralogical and hydrochemical investigations were carried out on cores from the confined Chalk aquifer in order to determine potential sources of fluoride. The cores were taken from boreholes at Longham, Blasford and Corfe Hills in the Wessex basin, relatively close to Lytchett Minster. The presence of fluorite (CaF_2), particularly along fracture surfaces, was confirmed in some samples. Furthermore, analysis of chalk pore waters indicated that fluoride concentrations in the matrix may be higher than in pumped groundwater. Based on these findings, three different chemical mechanisms were modelled, each one able to cause an increase in fluoride in the recovered water: 1) the fluoride concentration in the matrix is higher than in the fractures: the recovered water will reflect the difference in fluoride concentrations between the fracture water and the matrix water in the Chalk with no geochemical reactions occurring; 2) fluorite is available for dissolution in the matrix and in the fractures, but only a limited amount is present: the concentration of fluoride in the recovered water will be limited by the amount of fluorite in the sediment available for dissolution; 3) fluorite is available in sufficient quantities for the fluoride concentration to reach saturation but the reaction kinetics is slow: the rate of fluorite dissolution determines the fluoride concentration in the recovered water (for the dissolution kinetics, a simple reaction mechanism was assumed).

Table 3 Description of PHREEQC2 model runs for modelling fluoride concentrations in the recovered water at the ASR-site at Lytchett Minster.

Model run	Model name	Description
Sim Mixing	Simple Mixing	Behaviour of fluoride is conservative
Saturation	Saturation	Recovered water calcite/fluorite saturated
High Matr 1	High Matrix 1	Fluoride concentration in matrix 20% higher than in fractures
High Matr 2	High Matrix 2	Fluoride concentration in matrix 40% higher than in fractures
Kinetics 1	Kinetics 1	Rate of dissolution= k * (1-(Ca^{2+})(F^-)2/K) k=10^{-10}
Kinetics 2	Kinetics 2	Rate of dissolution= k * (1-(Ca^{2+})(F^-)2/K) k=$2*10^{-10}$
Kinetics 3	Kinetics 3	Rate of dissolution= k * (1-(Ca^{2+})(F^-)2/K) k=$4*10^{-10}$
Lim Av 1	Limited Availability 1	10 mg fluorite/ kg sediment can dissolve
Lim Av 2	Limited Availability 2	30 mg fluorite/ kg sediment can dissolve
Lim Av 3	Limited Availability 3	50 mg fluorite/ kg sediment can dissolve

Fig. 7 indicates the modelling results for the three different cases. It shows the relative increase in fluoride with respect to chloride during the recovery in year 2 of two consecutive one year ASR-cycles. The following conclusions can be made.

- Differences in fluoride concentration between the native water in the matrix and the fractures leads to a constant ratio between fluoride and chloride mixing during the recovery phase (>1 dependant on the matrix concentration of F) (Fig. 7A).

- Limited availability of fluorite leads to an excess of fluoride concentrations at the beginning of the recovery cycle. However, this excess is limited to a maximum ratio of 1.5 (Fig. 7B) and is expected to decrease further in subsequent ASR-cycles because the fluorite will be dissolved and flushed out during recovery.

- Kinetically determined fluoride concentrations show an excess in fluoride during the beginning of the recovery cycle, reducing to approximately 1 at the end of the recovery cycle. Depending on the rate constant, the initial relative mixing ratio fluoride/chloride can vary between 1 and >5 (Fig. 7C).

When comparing these results with the data from the field trial (Fig. 6) it can be concluded that differences in fluoride concentrations in the native water between the matrix and the fractures cannot explain the observed fluoride pattern during the different cycles from the field trial. Also, limited availability of fluorite for dissolution can only partly explain the observations because the field data do not indicate a decrease in slope of the fitted line in subsequent cycles. Therefore, it is concluded that the increase in fluoride is controlled by the dissolution kinetics of fluorite. If this is the case, a decrease in fluoride in subsequent cycles is unlikely to occur until available fluorite is exhausted and mechanism 2 becomes the predominant process. However, the amount of fluoride removed in solution during ASR-cycles is likely to be small compared with that present within the solid phases in the aquifer. Therefore, the viability of ASR under such conditions is limited unless additional measures are taken such as blending or removal of fluoride from the recovered water.

ASR-testing at Abberton, near Colchester (Essex and Suffolk water)

No testing has taken place so far.

ASR-testing at Great Horkesley (Anglian Water)

The issues described are taken from Golder Associates (1998).

An ASR-trial has been carried out lasting 60 days with one injection-recovery cycle. The target aquifer was the Chalk covered by Tertiary sand and gravels. Leakage from the Lower London Tertiary Sands was confirmed during the test. Diffusive exchange because of the dual porosity nature of the Chalk induced elevated sodium, potassium and ammonium concentrations in the recovered water. The quality of the recovered water was clearly influenced by both dual porosity exchange within the Chalk and leakage from the Tertiary layers as illustrated by elevated sulphate concentrations.

Apparently no pyrite dissolution or major anhydrite dissolution took place, although both minerals were present in the Chalk and/or Lower London Tertiaries.

3.4 The Lower Greensand

3.4.1 General

The Lower Greensand mainly consists of sand and sandstones with subsidiary argillaceous beds. In part of the aquifer, e.g. the Folkestone beds, relatively low pH and low alkalinity waters can be present.

3.4.2 Hydrogeochemical processes in the Lower Greensand

The main hydrogeochemical characteristics can be summarised (Edmunds et al., 1989):

- The formation is predominantly arenaceous, but important subsidiary amounts of silty and argillaceous material are also present. The rocks contain an important amount of glauconite, chert and ironstone and calcareous deposits also occur in small amounts.

- The overall carbonate content is low. In general waters from the Lower Greensand are undersaturated with respect to calcite and dolomite. At some places pH values less than 7 are observed. Under conditions of lower pH, some metals are mobile even under oxidising conditions.

- In the unconfined part of the aquifer, E_h values are highly positive; at greater depths more reducing conditions prevail and in the deepest wells sulphate reduction occurs indicating strongly reducing conditions.

- An increase in Na and Cl concentrations is observed in the deeper parts of the aquifer. This seems to be both a result of mixing with older formation water (Morgan-Jones, 1985) and, in the case of Na, some ion exchange.

With respect to trace element concentrations, the wide range of dissolved iron (and also manganese) concentrations in the Lower Greensand water has to be evaluated when planning ASR schemes.

At the ASR test-site at Stockbury the aquifer mineralogy of the Folkestone beds and part of the underlying Atherfield clay was investigated (CH2M Hill, 1999). The results can be summarised as follows:

- quartz dominates the aquifer ranging from 65 to 99%;
- pyrite is a major mineral ranging from traces to up to 8 %. It appears both as nodules and framboids and as a cement;
- calcite is present from trace amounts to 12 % of the sediment.

Other minor mineral phases include potassium feldspar, siderite, and phosphate nodules. The clays of the matrix and the clay layers in the formation are both dominantly weathered glauconite and kaolinite. The brown colour of the matrix present in some samples is due to iron-hydroxides.

3.4.3 Conceptualisation of the hydrogeochemistry of the Lower Greensand

The aquifer is regarded as a single porosity aquifer in which predominantly intergranular flow takes place. Therefore, it is more likely when executing ASR that a "bubble" of injected water will form around the ASR-injection well. This bubble, of almost 100 % native water, will be surrounded by a mixing zone of native and injected water. The creation of such a bubble (reservoir) of injected water in the aquifer has two major consequences.

- Simple mixing between the injected water and the native water will be restricted mainly to the mixing zone and therefore the impact of geochemical reactions due to mixing will be most important in the mixing zone, leaving the injected water in the bubble itself relatively unaffected.
- Almost pure injected water will be able to trigger more intense geochemical reactions with the sediment in the case of a large difference in quality between injected and native water.

Mixing modelling.

Based on the native groundwater quality data it seems that relatively oxidising conditions prevail, even in confined conditions. Other groundwater samples from the confined Lower Greensand (Edmunds et al., 1989) show that this is not the case everywhere in the confined Lower Greensand and often more reducing waters are present.

E_h conditions would allow for oxidation of available pyrite and this probably takes place on a limited scale. Because the injection waters are highly oxidising they might have the potential to oxidise pyrite, and possibly induce precipitation of iron oxides and hydroxides.

Due to the differences in the redox condition of the injected and native water, redox processes are likely to have a significant effect on recovered groundwater quality. A lowering of the groundwater pH might become an issue when the aquifer is poorly buffered in terms of pH. These issues were taken into account by executing three modelling scenarios:

In scenario 1, simple mixing was modelled. This implies that only chemical reactions as a consequence of the mixing of the two water samples were included. In the mixture, chemical equilibrium will be re-established and therefore the water quality might change. The type and impact of these chemical reactions depend on the composition of the mixture. Scenario 1 does not take into account any interaction with the aquifer sediment.

In scenario 2 mixing was modelled taking into account interaction with the sediment. The interaction with the sediment was modelled by including the following processes:

- saturation with iron-oxides and hydroxides
- saturation with pyrite
- saturation with siderite

In scenario 3 mixing was modelled taking into account interaction with the sediment as described for scenario 2, but it was also assumed that calcite was available in the sediment:

- saturation with iron-oxides and hydroxides
- saturation with pyrite
- saturation with calcite
- saturation with siderite

Due to the presence of clay layers and the presence of clay in the cement, more accurate modelling would require the incorporation of ion exchange processes and clay geochemistry. However, it is expected that incorporating these processes at this level of modelling would not significantly increase the reliability of the results. Clay related geochemistry was therefore not modelled.

Cycle modelling.

The ASR cycle was modelled as a 1-year cycle with an injection rate and recovery rate of 45 m^3/d. The injection period lasted for 4.1 months, the water was allowed to remain in the aquifer for 2.6 months after which a recovery period of 2.6 months followed by another standing period for 2.6 months was modelled. The dispersivity was set at 10 m. Since the input parameters are hypothetical, the modelled concentrations only indicate general trends in quality during ASR. The aquifer was modelled as a single porosity aquifer.

Chemical reactions taken into account were those resulting from simple mixing as a consequence of the injection of treated Upper Chalk groundwater in the Lower Greensand at Stockbury.

3.4.4 Selected water types

The quality of both the native and the injection waters are shown in Fig. 8, the analysis results are listed in Table 4 while the location of the native waters within their aquifers is shown in Fig. 2.

Native water

As an example, native groundwater from the ASR-trial at Stockbury in the Folkestone beds of the Lower Greensand was used.

Stockbury Lower Greensand water is undersaturated with respect to calcite. This indicates that further calcite dissolution is possible. The water also contains high iron concentrations (1.56 mg/l) which are likely to be the result of the dissolution of pyrite (and probably siderite) and is at saturation with respect to iron hydroxides.

Injection water

Two water types were identified as potential injection waters: Upper Chalk water taken from the Stockbury Upper Chalk production boreholes and surface water from a lowland river. As an example of lowland river water, water from the river Medway was chosen.

The Stockbury Upper Chalk water has been treated and is nearly at saturation with respect to calcite and saturated with respect to quartz. The pH of 6.98 is stabilized by the high alkalinity. The water is highly oxidising, saturated with oxygen and contains some nitrate.

The water of the river Medway is assumed to be at saturation with oxygen and has elevated nitrate concentrations (23 mg NO_3/l).

3.4.5 Results

Mixing modelling

The modelled effects using the different injection and native water on the recovered water quality are shown in Table 4. Injection of the Chalk injection water and the river Medway water in the Lower Greensand at Stockbury are modelled.

In Fig. 9 the evolution of pH and the dissolved iron concentration are illustrated for both cases. The simple mixing line, and the two mixing + equilibrium lines indicate a range within which the real concentration is likely to be found.

The main issues are:

- The high dissolved iron concentrations in the native water might lead to elevated dissolved iron concentrations in the recovered water because of mixing. However, because the Lower Greensand is a single porosity aquifer, mixing effects may be restricted to the mixing zone surrounding the injected water bubble in the aquifer. Therefore, the effects on the recovered water might be minimal if the injected amount exceeds the recovered amount. Furthermore, the dissolved iron might precipitate as iron oxide and hydroxide when the native water comes into contact with the oxidised injection water.

- In the modelled cases, no significant drop in pH was observed. A significant increase in the acidity could trigger desorption of heavy metals and might result in significant heavy metal concentrations in the recovered water. Since other water types in the Lower Greensand have very low bicarbonate concentrations (Edmunds et al., 1989) their buffering capacity might be minimal and when using such injection waters lowering of the pH cannot be excluded.

- Since pyrite is expected to be present in the Lower Greensand and is probably available for dissolution, an increase in dissolved iron as a result of pyrite oxidation by the dissolved oxygen present in the injection water is possible. However, the dissolved iron will precipitate as iron hydroxides, depending on the oxidising capacity of the injection water; also precipitation of siderite is possible. The increase in dissolved iron might then be restricted, but precipitation of iron hydroxides might cause clogging around the well. Also sulphate might increase as a consequence of pyrite oxidation, however the relative increase taken into account the high drinking water standard, is likely to be insignificant.

- The high nitrate concentrations in the injected water are likely to get reduced prior to recovery as a result nitrate reduction.

Example of cycle modelling

Modelling results for pH, nitrate, sulphate and iron are shown (Fig. 10). Because the aquifer is porous and the injected amount is larger than the recovered amount, the influence of the native water and the geochemical reactions due to mixing of the injected and the native water are only visible at the end of the recovery phase and the subsequent standing period.

Because the mixture mainly contains injection water and the injection water is oxidising, the injection water and the sediment are far from equilibrium leading to important quality changes if reactions with the sediment are taken into account.

3.4.6 Applications of ASR in the Lower Greensand

Awaiting update/further information on the actual situation of the ASR-scheme.

Table 4 Hydrochemical data used for the Lower Greensand modelling.

		NATIVE GROUNDWATER	INJECTION WATER	
		Stockbury CH2MHill XY: 161 584	**Treated Upper Chalk Water** CH2MHill	**Treated River Medway Water** Southern Water
Parameter	**Units**			
Temperature	C	16.1	10.8	?
pH		7.2	6.98	7.4
Dissolved Oxygen	mg/l	0	10.5	11.3*
E_h	mV	321	854	
Bicarbonate	mg/l			
Alkalinity	mg CaCO3/ l	107	258	110
Potassium	mg/l	2.4	1.1	4.9
Sodium	mg/l	9	10	41.2
Calcium	mg/l	39	110	66.6
Magnesium	mg/l	5.9	2.4	6.2
Iron	mg/l	1.56	n.d.	n.d.
Sulphate	mg/l	16	110	74
Nitrate	mg N/l	n.d.	3.75	5.2
Nitrite	mg N/l	n.d.	n.d.	?
Ammoniacal N	mg N/l	0.1	n.d.	?
Chloride	mg/l	19	19	47
Fluorite	mg/l	0.167	0.107	?
Silica	mg/l	16	9.1	?
Dominant redox couple to calculate E_h		n.a.	n.a.	O(-2)/O(0)
Mass balance		-1.62	1.69	-14.74
Saturation indices				
Calcite		-0.63	-0.16	0.16
Quartz		0.52	0.37	n.a.
Siderite		-0.63	n.a.	n.a.
Ferric hydroxide		3.35	n.a.	n.a.

* assumed at saturation

Table 5 Overview of the impacts of ASR in the Lower Greensand using the selected water types.

	Injection Waters	
Native Groundwater	GROUNDWATER EXAMPLE Stockbury Upper Chalk Injection Water	SURFACE WATER EXAMPLE River Medway water
Stockbury Lower Greensand water	*General Issues* • The original high iron concentrations in the native water might diminish because of the precipitation of iron oxide and hydroxide when oxidising conditions in the aquifer prevail due to the injection of oxidised water. Clogging problems are therefore possible. However, because the Lower Greensand is a single porosity aquifer, mixing effects may be restricted to the mixing zone surrounding the injected water bubble in the aquifer. Therefore, the effects on the recovered water might be minimal if the injected amount exceeds the recovered amount. Furthermore, the dissolved iron might precipitate as iron oxide and hydroxide when the native water comes into contact with the oxidised injection water. • The high pyrite content in the aquifer makes is likely that some pyrite dissolution will occur during the injection of oxidised water. This might induce increased sulphate concentrations (max 15 mg/l) and increased iron concentrations in the recovered water. The dissolved iron concentrations might subsequently diminish by the precipitation of iron oxides and hydroxides and/or the precipitation of siderite. This can lead to chemical clogging. Therefore significant iron concentrations in the recovered water cannot be excluded. • None of the modelled scenarios showed a significant lowering of the pH. Therefore no increase in heavy metal concentrations is expected as a consequence of pyrite oxidation. Since other water types in the Lower Greensand have very low bicarbonate concentrations (Edmunds et al., 1989) their buffering capacity might be minimal and when using such injection waters lowering of the pH cannot be excluded. • The high nitrate concentrations in the injected water are likely to get reduced prior to recovery as a result nitrate reduction. • Nitrate as well as dissolved oxygen are likely to diminish or, if pyrite oxidation is significant, completely disappear in the recovered water.	

3.5 The Permo-Triassic Sandstone Aquifer

3.5.1 General

The Permo-Triassic sandstones provides important groundwater resources, especially in northern and central England, where the Sherwood Sandstone Group forms the most important aquifer (Allen et al., 1997). Cases described in this study all refer to the Sherwood Sandstone Group.

3.5.2 Hydrogeochemical processes in the Sherwood Sandstone Aquifer

Groundwater in the aquifer is generally oxidising beneath outcrop in areas which are relatively drift free and the waters are relatively young. Where the Sherwood Sandstone becomes confined beneath the Mercia Mudstone a redox boundary is reached beyond which the groundwaters become increasingly reduced. The waters in the confined aquifer increase with age down dip and palaeowaters are present in the deepest parts of the aquifer.

Edmunds et al. (1982) concluded for the East Midlands Triassic Groundwater that the water quality evolution is dominated by carbonate and sulphate mineral solution and precipitation and redox reactions; cation exchange reactions are negligible and the hydrogeochemistry has evolved in the absence of residual saline water. Three distinct zones are recognised:

- recent groundwater (mainly < 100 y), oxidising, dominated by congruent dissolution of dolomite and by inputs from atmospheric and anthropogenic sources;
- groundwater age 10^3-10^4 y, predominantly reducing, dominated by incongruent dissolution of dolomite;
- groundwater age > 10^4 y, reducing conditions, approach to isotopic and chemical equilibrium in the carbonate system, dominance of gypsum dissolution.

The Sherwood Sandstone is dominated by sub-angular to rounded quartz grains, although sodic plagioclase, orthoclase and microcline have been recognised as both detrital minerals and late overgrowths (Edmunds et al., 1982; Smedley and Brewerton, 1997). Clay and marl horizons are also abundant and the sandstone is micaceous in parts. Red colouration throughout the sequence is due to the presence of iron oxides (haematite, goethite, limonite), usually as sand coatings and in argillaceous fractions. A total iron concentration in the range 0.5-3 weight % (as Fe_2O_3) can be observed at some places in the East Midlands.

The sandstone is commonly poorly cemented and unconsolidated near the surface but in parts contains a calcite cement. The cement may be gypsiferous in places. Dolomite is an important primary accessory mineral. The sandstone typically contains a total carbonate concentration of around 1-4 weight % (as CO_3). Pyrite has been recorded, notably in the uppermost part of the formation, although occurrences are rare (Edmunds et al., 1982).

3.5.3 Conceptualisation of the hydrochemistry of the Sherwood Sandstone

Mixing modelling

Three scenarios were modelled depending on the part of the aquifer in which the ASR-scheme is to be implemented:

For scenario 1 simple mixing was modelled. No interaction with the sediment of the aquifer took place.

Scenario 2 reflects the injection in the oxidising part of the aquifer where recent waters are present and includes interaction with the sediment. This scenario is only modelled with the recent native groundwater water from the borehole at Budby, Nottinghamshire.

The assumptions were:

- equilibrium with iron oxide and iron hydroxide
- equilibrium with calcite and dolomite

Scenario 3 reflects the injection in the reducing, more evolved part of the aquifer where palaeowaters are present and includes interaction with the sediment. This scenario is only modelled with the evolved native ground water from the borehole at Gainsborough.

The assumptions were:

- equilibrium with iron oxide and iron hydroxide
- equilibrium with calcite and dolomite
- dissolution of K-feldspar
- dissolution of pyrite
- dissolution of gypsum
- equilibrium with siderite

Cycle modelling

The ASR cycle was modelled as a 1-year cycle in the same way as described earlier for the Chalk.

Although the behaviour of the Sherwood Sandstone lies somewhere between dual-porosity (the bulk of the flow takes place in the fractures and storage is provided by the matrix) and single-porosity (flow takes place in the matrix), it is probably best described as a dual-permeability medium. The matrix is permeable enough to transmit water at the low rates which are relevant in regional flow systems, but probably not in some near-well situations where fracture flow is likely to dominate. Because mixing will be more intensive in the dual porosity case, this case is seen as the worst case and only the dual porosity case is modelled. The porosity of the fractures is assumed to be 1% and the matrix porosity 15%. The value of the exchange coefficient is assumed to be the same as the value calibrated for the Chalk, being $5\ 10^{-8}\ s^{-1}$ (Gaus *et al.*, 2000).

Cycle modelling was completed using injection of River Derwent water into the more evolved part of the Sherwood Sandstone aquifer (using the Gainsborough B.P. native water) and chemical reactions taken into account were those resulting from simple mixing.

3.5.4 Selected water types

The hydrochemical data for all the water types are listed in Table 6; the location of the native waters within their aquifers is shown in Fig. 2. A Piper diagram of all the samples is shown in Fig 11.

Native groundwater

Two typical examples of native water from the Sherwood Sandstone aquifer were chosen.

The sample taken at Budby is a relatively young groundwater. The water is moderately oxidising (E_h = 279 mV) as it is saturated with oxygen and contains elevated nitrate concentrations. It is undersaturated with respect to dolomite, slightly undersaturated with respect to calcite and saturated with respect to iron oxide. Both nitrate and chloride are likely to be influenced by human activities.

The sample taken at Gainsborough B.P. is much older. It is less oxidising (E_h=78 mV) and is depleted of oxygen while low concentrations of nitrates were measured. Dissolved iron and sulphates are present in high concentrations probably as a consequence redox reactions and dissolution of gypsum.

Injection water

Two water types were identified as potential injection waters in the Sherwood Sandstone aquifer: surface water from the river Derwent (median values measured at Bubwith for the period 1993-96 (Neal & Robson, 2000) and groundwater from the Magnesian Limestone Aquifer (Gaus et al., 2000).

The water of the river Derwent (untreated) is at saturation with respect to calcite and dolomite. The pH of 7.9 is buffered by the high alkalinity. The water is highly oxidising and contains low levels of nitrate.

The groundwater from the Magnesian Limestone aquifer is at saturation with respect to quartz, close to saturation with respect to calcite and slightly undersaturated with respect to dolomite. The water is depleted of oxygen and contains no nitrate. It also contains high strontium and barium concentrations (4.88 mg/l and 0.119 mg/l respectively).

3.5.5 Results

Mixing modelling

The modelled qualities of the recovered water when using the different injection and native waters are described in Table 7. Injection of both the surface water from the river Derwent and the groundwater from the Magnesian Limestone aquifer into the Sherwood Sandstone aquifer are modelled.

In Fig. 12 the evolution of pH and the dissolved iron concentrations are illustrated for each of the four cases. The simple mixing line and the mixing + equilibrium line are shown. As stated earlier the equilibrium assumptions for injection in the oxidising part of the aquifer (using the Budby 2 groundwater) and the reducing, more evolved part of the aquifer (using the Gainsborough B.P. groundwater) are different.

Example of cycle modelling

Modelling results for pH, iron, sulphate and magnesium are shown (Fig. 13). It is clear that in the modelled case the chemical reactions have more impact on the concentration of the shown parameters than the dual porosity effects. The increase in iron due to pyrite dissolution (if present) and sulphate and magnesium as a consequence of both dissolution of gypsum and dolomite (if present) will have a large impact on the quality of the recovered water.

Table 6 **Hydrochemical data used for the Sherwood Sandstone modelling.**

		NATIVE GROUNDWATER		INJECTION WATERS	
		Old SS water Gainsborough, B.P. Edmunds et al. (1982) XY: 482 390	**Recent SS water** Budby Edmunds et al. (1982) XY: 460 370	**Magnesian Limestone Water** South Nottinghamshire	**River Derwent Water** Neal & Robson (2000) median values
Parameter	**Units**				
Temperature	C	15.9	9.73	11.2	10
pH		7.57	7.68	7.4	7.86
Dissolved Oxygen	mg/l	0	9.7	0	11.3*
E_h	mV	78	279	154	n.d.
Bicarbonate	mg/l	172	117	252	
Alkalinity	mg CaCO3/ l				321
Potassium	mg/l	5.8	1.3	5.1	3.4
Sodium	mg/l	23	38	16.8	19.5
Calcium	mg/l	129	59	55	97.8
Magnesium	mg/l	27	29	36	8.55
Iron	mg/l	1.97	0.015	0.02	0.034
Sulphate	mg/l	365	92	26.8	93
Nitrate	mg N/l	0.06	7.23	n.d.	4.07
Nitrite	mg N/l	n.d.	n.d.	n.d.	0.0375
Ammoniacal N	mg N/l	n.d.	n.d.	n.d.	0.051
Chloride	mg/l	11	94	57	38
Fluoride	mg/l	0.078	0.047	n.d.	n.d.
Silica	mg/l	n.d.	n.d.	5.53	6.62
Dominant redox couple to calculate E_h		n.a.	n.a.	n.a.	O/O(-2)
Mass balance		-4.16	0.78	4.53	0.09
Saturation indices					
Calcite		0.16	-0.23	-0.18	0.42
Dolomite		-0.14	-0.64	-0.4	2.31
Quartz		n.a.	n.a.	0.15	-0.09
Gypsum		-0.93	-1.71	n.a.	n.a.
Ferric hydroxide		1.09	1.86	-0.48	8.2

* assumed at saturation

Table 7 **Overview of the impacts of ASR in the Sherwood Sandstone using the selected water types**

	Injection Waters	
Native Groundwater	GROUNDWATER EXAMPLE Magnesian Limestone Water	SURFACE WATER EXAMPLE River Derwent Water
Recent Sherwood Sandstone water (Budby)	*General* • Nitrate concentrations might increase due to mixing with the high nitrate native water • No major changes in pH are expected, maximum pH range is 7.6- 8. The waters are likely to be slightly basic in all modelled cases and with a high buffering capacity due to the high alkalinity, the pH is likely to be relatively stable.	
		Specific • An increase in Mg concentration is expected if dolomite dissolves.
Old Sherwood Sandstone water (Gainsborough, B.P.)	*General* • No major changes in pH are expected, maximum pH range is 7.6- 8. The waters are likely to be slightly basic in all modelled cases and with a high buffering capacity due to the high alkalinity, the pH is likely to be relatively stable. • An increase in dissolved iron above the standard in the recovered water due to mixing with the high iron native water is possible. A further important increase (up to several mg) can take place if pyrite is available for oxidation. • Higher sulphate concentration in the native water might lead to increased sulphate concentration in the recovered water if important mixing occurs. • A further increase in sulphate concentration is possible if dissolution of gypsum occurs. This might induce precipitation of calcite and dissolution of dolomite. Also Ca-concentrations will increase significantly. • A significant increase in magnesium might be expected when dolomite dissolves as equilibrium with gypsum and pyrite is established.	
		Specific • A decrease in oxygen and nitrate (apart from mixing with the low-nitrate native water) is expected only when pyrite is available for oxidation.

3.5.6 Applications of ASR in the Sherwood Sandstone aquifer.

ASR-trials are ongoing in Nottinghamshire where Lower Magnesium Limestone water is injected in the Sherwood Sandstone aquifer. At Loftsome Bridge treated river Derwent water is also being injected for ASR-purposes in the Sherwood Sandstone aquifer at a trial site being investigated by Yorkshire Water plc.

3.6 The Jurassic Limestone Aquifer

3.6.1 General

The Jurassic Lincolnshire Limestone is of major importance in Eastern England. Groundwater flow is mainly controlled by secondary porosity through an extensive interconnected fissure system. However, the matrix in certain facies is relatively porous and groundwater flow through these deposits is intergranular (Edmunds at al., 1989).

3.6.2 Geochemical processes in the Lincolnshire Limestone

The geochemistry of the Lincolnshire Limestone groundwater has been extensively described (Edmunds et al., 1989). The main hydrogeochemical changes taking place as the groundwater evolves within the aquifer are:

- Carbonate reactions take place rapidly during groundwater recharge, and the water quickly reaches saturation with respect to calcite, probably in the unsaturated zone;

- Above the clearly distinguished redox boundary dissolved oxygen persists and nitrate remains stable.

- Beyond the redox boundary, nitrogen and oxygen quickly disappear. The progress of the groundwater downgradient is marked by an increase in pH and also the start of a decrease in Ca and corresponding increase in HCO_3 and Na as a consequence of ion exchange reactions.

- The increase in bicarbonate is partly at the expense of organic matter and is coincident with the reduction of sulphate.

Chemical analysis of limestone core (Lewin, 1988) suggest that the rock can be divided into oolitic limestones and argillaceous limestones. The presence of dolomite is not significant on a formation-wide scale. Organic carbon may form up to 5% by weight of the limestone (Bishop & Lloyd, 1990).

With respect to the minor elements, fluoride and iron may reach concentrations above water quality standards on a wide scale in the aquifer. High iron concentrations are related to the reducing conditions in the aquifer, whilst high fluoride concentrations appear to result from dissolution of fluorapatite or fluorite present as trace minerals in the limestone (Edmunds et al., 1989).

3.6.3 Conceptualisation of the hydrochemistry of the Lincolnshire Limestone

Mixing Modelling

Two scenarios were modelled:

For scenario 1 simple mixing was modelled. No interaction with the sediment of the aquifer took place.

Scenario 2 reflects interaction with the sediment. The only assumption was that equilibrium was established with calcite. Although ion exchange might also have an influence it was not modelled because of the lack of information on the exchangeable ions sorbed to the sediment.

Cycle modelling

The ASR cycle was modelled as a 1-year cycle with the same specifications as described earlier for the Chalk. Since the input parameters are hypothetical, the modelled concentrations only indicate general trends in quality during ASR.

The porosity of the fractures is assumed to be 2.5% and the matrix porosity 5%. The value of the exchange coefficient is assumed to be the same as the value calibrated for the Chalk, $5*10^{-8}$ s^{-1} (Gaus *et al.*, 2000). Chemical reactions taken into account were those resulting from simple mixing as a consequence of the injection of River Trent water in the more evolved part of the Lincolnshire Limestone aquifer (using the Spalding Bulb Co. borehole native groundwater).

3.6.4 Selected water types

The analysis data for all water types are listed in Table 8; the location of the native waters is shown in Fig. 2. A Piper diagram of all the samples is shown in Fig. 14.

Native water

Two examples of native water from the Lincolnshire Limestone aquifer were chosen.

The sample taken at Lenton Pumping Station (Lenton PS) is a recent groundwater. The water is at a neutral pH is oxidising (E_h= 411 mV) and saturated with oxygen and contains elevated nitrate concentrations (62.3 mg NO_3/l). It is close to saturation with respect to calcite and at saturation with respect to iron hydroxide. It is slightly undersaturated with respect to quartz.

The sample taken at Spalding Bulb Company (Spalding Bulb Co) is an older, more evolved water sample from the Lincolnshire Limestone aquifer. It is marked by a high pH (pH 9) and it is reducing (E_h=-120 mV). The sample is depleted in oxygen and nitrate. As a consequence of reducing conditions ongoing redox processes, the iron concentration is slightly elevated. Chloride and fluoride concentrations are high (688 mg/l and 5 mg/l respectively). The water is at saturation with respect to calcite, dolomite, and iron hydroxide and slightly undersaturated with respect to quartz and undersaturated with respect to fluorite.

Injection water

As an example of injection water, untreated surface water from the River Trent at Cromwell Lock was selected. The composition of the water used consisted of the median elemental concentrations measured during 1993-97 (Neal & Robson, 2000). This water is oxidising, saturated with oxygen and contains elevated nitrate concentrations. The pH of the water is slightly alkaline and at saturation with respect to calcite and dolomite. It is also saturated with respect to quartz.

3.6.5 Results

Mixing modelling

The modelling conclusions of ASR using one injection and two native waters are shown in Table 9.

In Fig. 15 the evolution of the pH and the nitrate concentration is illustrated for each case. The simple mixing line and the mixing + equilibrium line are shown.

Table 8 Hydrochemical data used for the Lincolnshire Limestone modelling

		NATIVE GROUNDWATER		INJECTION WATER
		Old LL water Spalding Bulb Co (no 30) Edmunds et al. (1982) TF 232 219	**Recent LL water** Lenton PS Edmunds et al. (1982) TF 055 313	**Surface water** River Trent (Cromwell Lock) Neal & Robson (2000) Median values
Parameter	**Units**			
Temperature	C	10.8	10.1	11
pH		9	7.1	7.96
Dissolved Oxygen	mg/l	0	6.7	11.3*
E_h	mV	-120	411	?
Bicarbonate	mg/l	521	276	
Alkalinity	mg CaCO3/ l			349
Potassium	mg/l	3.7	3.3	10.6
Sodium	mg/l	592	16	88
Calcium	mg/l	6	153	105
Magnesium	mg/l	4.3	6.7	24
Iron	mg/l	0.13	0.0006	0.032
Sulphate	mg/l	10	110	180
Nitrate	mg N/l	n.d.	14.07	8.58
Nitrite	mg N/l	?	?	0.093
Ammoniacal N	mg N/l	?	?	0.123
Chloride	mg/l	688	39	120
Fluoride	mg/l	5	0.014	?
Silica	mg/l	1.9	3.2	7.29
Dominant redox couple to calculate E_h		n.a.	n.a.	O/O(-2)
Mass balance		-4.37	4.71	-14
Saturation indices				
Calcite		0.6	-0.1	0.82
Dolomite		1.22	-1.43	1.14
Quartz		-0.35	-0.07	0.27
Gypsum		-3.86	-1.29	-1.29
Ferric hydroxide		0.16	0.26	2.23

* assumed at saturation

Table 9 **Overview of the impacts of ASR in the Lincolnshire Limestone using the selected water types.**

Native Groundwater	**Injection water**
	River Derwent Water
Recent Lincolnshire Limestone water (Lenton PS)	• No major changes in pH are expected, maximum pH range is 7.1-8.0. • Nitrate concentrations which are high in the native groundwater and elevated in the water from the river Trent are likely to be high in the recovered water.
Older Lincolnshire Limestone water (Spalding Bulb Co.)	• No major changes in pH are expected, maximum pH range is 8.0-9.0. • Injection into the Lincolnshire Limestone aquifer where it contains older water will possibly lead to a deterioration of the recovered water quality. Due to the dual porosity character of the Lincolnshire Limestone (which is however less explicit than for the Chalk aquifer), more intensive mixing between the native and the injection water can be expected and this might result in high concentrations of sodium, chloride as well as fluoride in the recovered water. • The slightly elevated iron concentrations in the native water are likely to reduce through oxidation when the oxidised water is injected. A decrease in nitrate concentrations in the recovered water might occur as a consequence of redox processes.

Example of cycle modelling

Modelling results for pH, nitrate, sulphate and chloride are shown (Fig. 16). Due to the low matrix porosity of the Lincolnshire Limestone the influence of dual porosity effects on the modelled concentrations is less than in the case of the Chalk and the Sherwood Sandstone. The shape of the curves is very similar to the shape of the curves for the Lower Greensand aquifer. It can therefore be concluded that in the Lincolnshire Limestone mixing effects will be intermediate between a dual porosity aquifer with large matrix porosity (such as the Chalk) and a single porosity aquifer. However, in cases where the native water contains high concentrations of unwanted elements, mixing will generally lead to a deterioration of the recovered water quality unless the injected amount of water exceeds the recovered amount by a significant amount. This is illustrated for fluoride.

4. CONCLUSIONS

To assess the likely chemical quality of the recovered water when planning an ASR-scheme three components have to be taken into account:

- chemical aspects of the injected water;
- chemical aspects of the native water in the aquifer;
- geochemistry of the aquifer and the chemical interaction with the injected water (e.g. dissolution of pyrite).

Major chemical changes to the quality of the injected water during recovery are expected when one or more of the following conditions are met:

- a large difference in chemical condition between the injected and the native water can cause large differences in pH or redox condition.
- the native water or the sediment do not possess a sufficient pH buffering capacity (e.g. in the case of acidic waters where no calcite is present for dissolution)
- there is a large difference in elemental concentrations between the injection and the native water (e.g. fluoride) and important mixing occurs (e.g. in dual porosity aquifers)
- a change in chemical condition of the water having contact with the sediment is able to trigger major (e.g. dissolution of gypsum) or minor (e.g. dissolution of heavy metals) reactions.

Thirteen different injection water/native water combinations for four aquifers (Chalk, Lower Greensand, Jurassic Limestones and Triassic Sandstones) were modelled (Table 10). The conclusions are based on the modelled cases only, and highlight the main chemical reactions likely to occur in implementing an ASR-scheme. Other chemical interactions may determine the recovered water quality when other injection waters are used, the native water has a different quality, or the geochemistry of the aquifer is different from the one assumed here. Also minor reactions and elemental concentrations have not been modelled.

Table 10 Overview of the injection and native water combinations used for the PREEQC2 mixing modelling.

Chalk	Lincolnshire Limestone
• Injection of treated Upper Chalk water into the confined Upper Chalk at Lytchett Minster • Injection of treated Upper Chalk water into the confined Upper Chalk at Holton Heath • Injection of treated Blashford Lakes surface water into the confined Upper Chalk at Lytchett Minster • Injection of treated Blashford Lakes surface water into the confined Upper Chalk at Holton Heath	• Injection of river Trent water into the Lincolnshire Limestone at Spalding Bulb Company • Injection of river Trent Water into the Lincolnshire Limestone at Lenton PS
Sherwood Sandstone	**Lower Greensand**
• Injection of river Derwent water into the Sherwood Sandstone aquifer at Budby. • Injection of river Derwent water into the Sherwood Sandstone aquifer at Gainsborough B.P. • Injection of Magnesian Limestone Water into the Sherwood Sandstone aquifer at Gainsborough B.P. • Injection of Magnesian Limestone Water into the Sherwood Sandstone aquifer at Budby.	• Injection of treated Upper Chalk water into the Lower Greensand at Stockbury • Injection of river Medway water into the Lower Greensand at Stockbury

In Table 11 the main chemical reactions are listed for each aquifer and are classified into issues related to the native water quality, issues related to the injected water quality and issues related to the chemical reactions within the aquifer. At the lower end of the figure the influence of the dual or single porosity character of the aquifer on the chemical reactions is indicated. Depending on the physical characteristics of the aquifer, different types of chemical interactions are likely to dominate the recovered water quality. In the case of a dual porosity aquifer, mixing between injection and native water will be intensive. Therefore the recovered water will contain a large component of the native water and will be influenced by the chemical interactions between the two water types. In the case of a single porosity aquifer, a bubble of injection water is likely to develop and mixing will be limited to the outer areas of the bubble. In this case, however, interaction between the injected water and the sediment will generally be more important than in the dual porosity case.

Within this study it was also clearly illustrated that the geochemical model can be used at different levels when planning an ASR-scheme. In the first stage, at the desk-study level, geochemical modelling can be used as a crude assessment of the chemical viability of the scheme. In a further stage of the ASR-scheme implementation, geochemical modelling can be supported by the observed data, used as a way of assessing the impact of specific geochemical reactions as illustrated for fluoride in the ASR-trial in the Chalk.

5. REFERENCES

Appelo CAJ & Postma D (1993). Geochemistry, groundwater and pollution. Balkema Rotterdam.

Bishop P K & Lloyd J W (1990). Chemical and isotopic evidence for hydrogeochemical processes occurring in the Lincolnshire Limestone. Journal of Hydrology 121, 293-320

CH2M Hill (1999). ASR investigation of the Lower Greensand Formation at Stockbury, Kent. Report prepared for Mid Kent Water PLC by CH2M Hill.

Edmunds W M, Cook J M, Kinniburgh D G, Miles, D L & Trafford J M (1989). Trace-element occurrence in British groundwaters. BGS Research Report SD/89/3.

Edmunds WM, Bath AH & Miles DL (1982). Hydrochemical evolution of the East Midlands Triassic sandstone aquifer, England. Geochimica et Cosmochimica Acta 46, 2069-2081.

Gaus I, Williams A T & Shand P (2000). Physical and geochemical modelling (SWIFT-PHREEQC) of British aquifers for aquifer storage and recovery purposes. BGS Technical Report WD/00/08.

Jones H K, Gaus I, Williams A T, Shand P & Gale I N (1999). ASR-UK. A review of status of research and investigations. BGS Technical Report WD/99/54.

Jones H K, Macdonald D M J & Gale I N (1998). The potential for aquifer storage and recovery in England and Wales. BGS Technical report WD/98/26.

Lewin K (1988). I.C.P. Analytical techniques applied to the hydrogeochemistry of the Southern Lincolnshire Limestone aquifer. Ph.D. Thesis, University of London.

Morgan-Jones M (1977). Mineralogy of the non-carbonate material from the Chalk of Berkshire and Oxfordshire, England. Clay Minerals 12, 331-344.

Neal C & Robson AJ (2000). A summary of river water quality data collected within the Land-Ocean Interaction Study: core data for eastern UK rivers draining to the North Sea. The Science of the Total Environment 251/252 (2000), 585-665.

Shand (1999). A geochemical investigation of chalk core samples from the pilot ASR boreholes in the southern Wessex basin. BGS Technical Report WD/99/55C.

Smedley P L & Brewerton L J (1997). The natural (baseline) quality of groundwaters in England and Wales. Part 2: the Triassic Sherwood Sandstone of the East Midlands and South Yorkshire. BGS technical Report WD/97/52.

Williams A T, Shand P & Gale I N (1999). Numerical and geochemical modelling of the ASR trial at Lytchett Minster, Dorset. BGS Technical Report WD/99/17C.