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Geochemical interactions between supercritical CO_2 and the Midale Formation. II: Preliminary test experiments - initial fluid chemistry data

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Key words

CO_2, carbon dioxide, storage, monitoring, Weyburn, Midale Formation, experimental study, geochemistry, fluid-rock interaction.

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Foreword

This report is the published product of a study by the British Geological Survey (BGS), and forms part of the international IEA Weyburn CO_2 Monitoring and Storage Project. This project aims to monitor and predict the behaviour of injected CO_2 in the Midale reservoir at the Weyburn field in southern Saskatchewan, Canada, using methods that include time-lapse geophysics, modelling its subsurface distribution and migration, and simulating likely chemical interactions with the host rock.

This report aims to provide an initial description of certain fluid chemical data from a series of test experiments that have been conducted within the Hydrothermal Laboratory of the British Geological Survey. These test experiments were undertaken to ascertain appropriate sampling frequencies for later experiments. The experiments utilised samples of 'Midale Marly' material from the Weyburn field, and reacted this under *in-situ* conditions with synthetic formation water (± CO_2).

Acknowledgements

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The authors would also like to thank researchers at the University of Calgary for information on the baseline formation water chemistry of the Weyburn oil field.

Finally, the authors would like to thank staff at Saskatchewan Energy and Mines for their help in the selection of samples of core material from their extensive collection of borehole cores form the Weyburn oil field.

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Summary

This report describes work undertaken at the British Geological Survey (BGS) that forms part of the international IEA Weyburn CO_2 Monitoring and Storage Project. This project aims to monitor and predict the behaviour of injected CO_2 into the Midale reservoir at the Weyburn oil field in southern Saskatchewan, Canada, using methods that include time-lapse geophysics, modelling its subsurface distribution and migration, and simulating likely chemical interactions with the host rock. This report aims to provide an initial description of certain fluid chemical data from a series of test experiments that have been conducted within the Hydrothermal Laboratory of the British Geological Survey. These test experiments were undertaken to ascertain appropriate sampling frequencies for later experiments. The experiments utilised samples of 'Midale Marly' material from the Weyburn field, and reacted this under *in-situ* conditions with synthetic formation water (± CO_2). The experimental techniques used are as detailed in Rochelle *et al.* (2002).

The experiments were conducted at 60°C and pressurised to 160 bar [16 MPa] using either CO_2 or N_2. Experiment durations ranged from one week to 10 weeks. Initial results show generally higher reaction in the CO_2 experiments compared to the N_2 experiments. They also show relatively rapid carbonate mineral reaction and slower silicate mineral reaction.

1 Introduction and preliminary information

The main aim of the test experiments detailed in this report was to help refine sampling techniques and constrain better the sampling frequencies of later experiments. However, they also produced analytical data, and these can be used to elucidate information about certain geochemical processes.

The following descriptions are only a preliminary interpretation of the fluid chemical data, and these may be refined in later reports in the light of increased knowledge about the processes involved. If mineralogical analysis of the solid reaction products is carried out, it will be reported elsewhere.

A detailed description of the experimental techniques used can be found in Rochelle *et al.* (2002), and only certain information specific to the test experiments is reported here. In summary, the experiments:

- were 'batch' type
- used a 10:1 fluid:rock ratio
- used crushed 'Midale Marly' at either 250-500 μm or <250 μm size fractions
- were run at 60°C
- were run at 160 bar [16 MPa]
- were pressurised with either CO_2 or N_2
- ran for between 1 and 8 weeks

The 'recipe' for the synthetic formation water is given in Table 1. This was based upon analyses of waters extracted from well 14-13-6-14W2 (Shevallier, pers. comm.). Other specific details for each experiment are given in Table 2.

Note that more than one type of identification code was used for the same Midale Marly sample. This reflects the history of the sample as it passed through various laboratories prior to use in the experiments:

- BGS2A. This code was assigned by staff at GEUS when the original sample plug was first drilled from the Weyburn core material (well 14-13-6-14W2, sample depth 1403.54 m).
- H636. This code was assigned by staff in the BGS mineralogical laboratories when the sample first arrived at the BGS. It is used to help keep track of all mineralogical analyses performed on the sample.
- HTL134. This code was assigned by staff in the BGS Hydrothermal Laboratory. It is used to help link all experiments using the same solid material.

The test experiments were designed to investigate both the rate of reactions and their possible end points. Determination of rate information was aided by using a fixed grain size that had been cleaned of fine material (250-500 μm). This relatively large grain size would have limited the surface area available for reaction, and hence acted to slow dissolution processes to rates more conducive to this study. Conversely, high surface areas would aid the achievement steady-state conditions in shorter timescales. Therefore, some experiments utilised a finer fraction (<250 μm). However, only 2 experiments were conducted with the high surface area (<250 μm) material, and so it is not possible to say at this stage whether steady-state conditions were actually achieved. What is apparent however, is that the '<250 μm' experiments represent systems that are more likely to be close to steady-state conditions compared to the '250-500 μm' experiments.

The test experiments were run at 160 bar [16 MPa] utilising ISCO syringe pumps, which proved to be reliable. However, future longer-term experiments will require the use of a single stage gas regulator to maintain nitrogen pressure (as a consequence of equipment commitments). Two such regulators were tried during the period of the test experiments, and it was found that they were only reliable up to 150 bar [15 MPa] (even though the manufacturer indicated otherwise). Therefore, future experiments are likely to be run at 150 bar [15 MPa], which is still within realistic bounds of actual *in-situ* pressures in the Weyburn field. The impact of N_2 pressure was scoped by conducting one experiment at atmospheric pressure (i.e. having a huge pressure difference between it and the rest of the N_2 experiments).

Pressure control for future CO_2 experiments will remain via an ISCO syringe pump. This is because it gives slightly better pressure control, which is important because it impacts upon CO_2 solubility (e.g. Toews *et al.*, 1995) and, as a consequence, pH and reactivity towards carbonate minerals.

2 Results

Analysed fluid compositions are given in Appendixes 1 and 2, together with comments supplied by the BGS analytical chemists. A few of the analytes show useful trends, and these are expanded upon below.

Not all analytes show definite trends in concentration over time. There are various reasons for this, which could include:

- Some reactions were so fast that they had achieved steady-state within the minimum sampling time (1 week).
- Some reactions were so slow that they had not had long enough to cause a measurable change in solution composition over the maximum sampling time (10 weeks).
- Inter-sample variation was larger than any actual changes in fluid composition.

In interpreting what may have occurred within the experiments, it is important to be aware of the minimum resolution in concentration between any two solutions. This 'analytical uncertainty' will increase towards the instrumental detection limit. Also, although actual instrument detection limits may be low, they may be greatly increased in practice, especially if solutions have to be diluted to a significant extent. These factors have to be borne in mind when interpreting the data (for further comments see Rochelle *et al.*, 2002).

For the analyses presented in Appendixes 1 and 2, sub-samples were diluted 50 times prior to analysis, except for TIC/TOC analyses, where a 20 times dilution was used, and for pH/alkalinity, where an undiluted sub-sample was used.

The following sections attempt to describe potential reactions occurring due to the presence of CO_2. However, the N_2 experiments also allow the possibility of checking whether the starting fluid (and hence the fluid actually sampled at the well) is in equilibrium with the minerals in the Midale Marly Formation. The descriptions do not cover all analytes, but only those where some initial conclusions can be reached. Insights based on data from future experiments may allow for more detailed conclusions to be drawn.

Sodium

The data for Na are shown in Figure 1.

The initial synthetic formation water may have a slightly higher Na concentration compared the original University of Calgary analysis from well 14-13-6-14W2, though the difference is barely outside the analytical error.

The data show very similar behaviour of Na in both CO_2 and N_2 experiments. This suggests that the processes governing Na reactivity are not influenced by the presence of CO_2.

At first glance, the data *appear* to show a slow decrease over 9 weeks. However, if a value of ±5% uncertainty is assumed for the data (equating to approximately ±1400 mg l^{-1}), then all the data from the experiments would actually be equivalent. A maximum value of ±5% uncertainty is probably not unrealistic given the large dilution factors that were applied to the solutions prior to analysis.

If the actual uncertainty in the data is in fact <±5% (possible, as the ±5% value is considered an upper estimate), there may indeed be a slow decrease in Na concentration over time. It is possible that this represents uptake of Na by the Midale Marly sample (for example through ion exchange onto clay phases) as it tries to equilibrate with the solution. The direction of this reaction would not be in disagreement with the notion that the Na concentration in the starting synthetic formation water is representative of a realistic *in-situ* fluid composition.

Magnesium

The data for Mg are shown in Figure 2.

The initial synthetic formation water has essentially the same Mg concentration as the original University of Calgary analysis from well 14-13-6-14W2 (within analytical error).

The data show quite different behaviour of Mg between the CO_2 and N_2 experiments. This suggests that the presence of CO_2 has a large impact on the processes governing Mg reactivity.

Overall, the CO_2 experiments show a 'decelerating' increase in Mg concentration from a starting value of approximately 450 mg l^{-1} [c. 1.85×10^{-2} mol l^{-1}] to approximately 710 mg l^{-1} [c. 2.92×10^{-2} mol l^{-1}] over 8 weeks. This increase is greater than any ±5% uncertainty (equating to approximately ±35 mg l^{-1}) and so reflects a real increase in Mg concentration. The increase is interpreted as resulting from the dissolution of Mg-rich carbonate (e.g. dolomite). The general shape of the concentration profile suggests that a steady-state concentration of approximately 710 mg l^{-1} was achieved after approximately 1000 hours. Note that these conclusions effectively ignore the data point of 660 mg l^{-1} after approximately 1300 hours, which may be an unduly low concentration.

The initial rate of Mg release in the 'CO2+grains' experiments averaged over the first 5 days is calculated to be 6.26×10^{-10} mol s^{-1}. For a 5g sample of Midale Marly used in the experiments, this equates to 1.25×10^{-10} mol g^{-1} s^{-1}. N_2 BET measurements of the 250-500 μm sample of Midale Marly used, give a value of 0.65 $m^2 g^{-1}$. Consequently, the initial rate of Mg release can be expressed as 1.93×10^{-10} mol cm^{-2} s^{-1}.

Interpretation of the data for the N_2 experiments is less straightforward as there is no clear concentration profile to the data. This is mainly due to the differences between the two data points at approximately 1800 hours. Although it is not possible to say with absolute certainty, it is possible that there was minor dissolution of Mg-rich carbonate, at least over shorter (<500 hours) timescales. Information from later experiments might help resolve whether dissolution occurs or not. However, from a qualitative standpoint, it is apparent that the Mg concentration in all the N_2 experiments is *at least approximately* representative of formation water from well 14-13-6-14W2.

Calcium

The data for Ca are shown in Figure 3.

The initial synthetic formation water appears to have a slightly lower Ca concentration compared to the original University of Calgary analysis from well 14-13-6-14W2 (by about 11%). The reasons for this are unclear at this time.

The data for Ca are more problematic than for Na and Mg, though the data from the N_2 experiments appear to be the more consistent than those from the CO_2 experiments.

The data for the CO_2 experiments do not show a clear concentration profile. Intermediate timescale data (at approximately 500 and 1000 hours) appear to indicate that dissolution of a Ca-rich phase (e.g. calcite) had occurred, raising Ca concentrations from approximately 1140 mg l^{-1} [c. 2.84×10^{-2} mol l^{-1}] to approximately 1770 mg l^{-1} [c. 4.42×10^{-2} mol l^{-1}]. However, shorter and longer timescale data show no real difference in concentration from the starting fluid. Although enhanced dissolution was expected in the presence of CO_2, detailed conclusions are reserved until data from future experiments can be assessed. One possibility currently being considered is that rapid carbonate precipitation occurred (either within the experiment during sampling/depressurisation or within the stored samples), leading to erroneously low concentrations. If this were the case, then the 3 lower value data points would be considered highly 'uncertain'.

The data for the N_2 experiments are more consistent. It is possible that there was minor dissolution of Mg-rich carbonate, at least over shorter (<500 hours) timescales. However, over longer timescales the experiments appear to reach steady-state, with concentrations virtually identical to the starting fluid. It therefore appears that the Ca concentration in the starting synthetic formation water is representative of a realistic *in-situ* fluid composition.

Strontium

The data for Sr are shown in Figure 4.

The initial synthetic formation water appears to have a significantly higher concentration compared to the original University of Calgary analysis from well 14-13-6-14W2 (by about twice). The reasons for this are unclear at this time.

The data show very similar behaviour of Sr in both CO_2 and N_2 experiments. This suggests that the processes governing Sr reactivity are not influenced by the presence of CO_2.

The data for both the CO_2 and the N_2 experiments appear to show a rapid decrease in Sr concentration from a starting value of approximately 90 mg l^{-1} [c. 1.03×10^{-3} mol l^{-1}] within the first few days of the experiments. Subsequently, Sr concentrations remain roughly constant at approximately 50 mg l^{-1} [c. 5.71×10^{-4} mol l^{-1}]. This latter concentration is reasonably representative of 14-13-6-14W2 well water.

Silica

The data for Si are shown in Figure 5.

The Si concentration was below detection for the sample of starting fluid whose data are plotted in the Figures 1-5. However, a similar sample gives a concentration of 4.61 mg l^{-1} (see Appendixes 1 and 2). Such an inter-sample variation may reflect the impact of large dilution factors and analysing solutions close to the detection limits of the ICP. That being said, the starting solution appears to have a lower Si concentration within it compared to the original University of Calgary analysis from well 14-13-6-14W2.

The data show quite different behaviour of SiO_2 between the CO_2 and N_2 experiments. This suggests that the presence of CO_2 has a large impact on the processes governing SiO_2 release.

Overall, the CO_2 experiments show an increase in SiO_2 concentration over time. This is likely to be due to dissolution of Si-rich minerals within the Midale Marly sample. Between weeks 1 and 8 there was a steady increase in SiO_2 concentration (in the 250-500 μm size fraction experiments) from 9.3 mg l^{-1} [c. $3.31\text{x}10^{-4}$ mol l^{-1}] to 13.4 mg l^{-1} [c. $4.77\text{x}10^{-4}$ mol l^{-1}]. The steady release rate of Si is calculated to be $1.72\text{x}10^{-12}$ mol s^{-1}. For a 5 g sample of Midale Marly this equates to $3.44\text{x}10^{-13}$ mol g^{-1} s^{-1}. N_2 BET measurements of the 250-500 μm sample of Midale Marly used, give a value of 0.65 m^2g^{-1}. Consequently, the initial rate of Si release can be expressed as $5.29\text{x}10^{-13}$ mol cm^{-2} s^{-1}.

The CO_2 experiment containing a much higher proportion of fine material (<250 μm size fraction) gave a final SiO_2 concentration of 17.3 mg l^{-1} [c. $6.16\text{x}10^{-4}$ mol l^{-1}], which is consistent with the experiments containing the coarser size fraction. It is unclear however, whether this represents a steady-state concentration. Subsequent, longer-term experiments with Midale Marly material may resolve this issue.

The data for the N_2 experiments appear to indicate steady-state conditions, with concentrations virtually identical to the starting fluid. It therefore appears that the SiO_2 concentration in the starting synthetic formation water is representative of a realistic *in-situ* fluid composition.

3 Conclusions

A preliminary experimental study has been undertaken to react CO_2 with samples of 'Midale Marly' and a synthetic formation water. These were reacted at 60°C and at 160 bar [16 MPa] – representative of in-situ conditions. Non-reacting experiments pressurised with N_2 were also undertaken. The aim of this study was to provide an initial description and quantification of important fluid-mineral reactions to help define sampling intervals for future experiments.

Overall, the experiments proved successful. They remained intact over several weeks, useable samples could be extracted, and preliminary fluid analyses indicate that discernable changes in fluid chemistry can be made.

Preliminary results show generally higher reaction in the CO_2 experiments compared to the N_2 experiments. They also show relatively rapid carbonate mineral reaction and slower silicate mineral reaction. Release rates were calculated: for Mg (representing carbonate mineral dissolution) this was $1.93\text{x}10^{-10}$ mol cm^{-2} s^{-1}, and for Si (representing silicate mineral dissolution) this was $5.29\text{x}10^{-13}$ mol cm^{-2} s^{-1}.

References

Rochelle, C.A., Birchall, D.J. and Bateman, K. (2002). Geochemical interactions between supercritical CO_2 and the Midale Formation. I: Introduction to fluid-rock interaction experiments. British Geological Survey Commissioned Report, CR/02/289, 28 p.

Toews, K.L., Shroll, R.M. and Wai, C.M. (1995). pH-defining equilibrium between water and supercritical CO_2. Influence on SFE of organics and metal chelates. Analytical Chemistry, 67, 4040-4043.

Figure 1 Variation of measured Na concentrations over time.

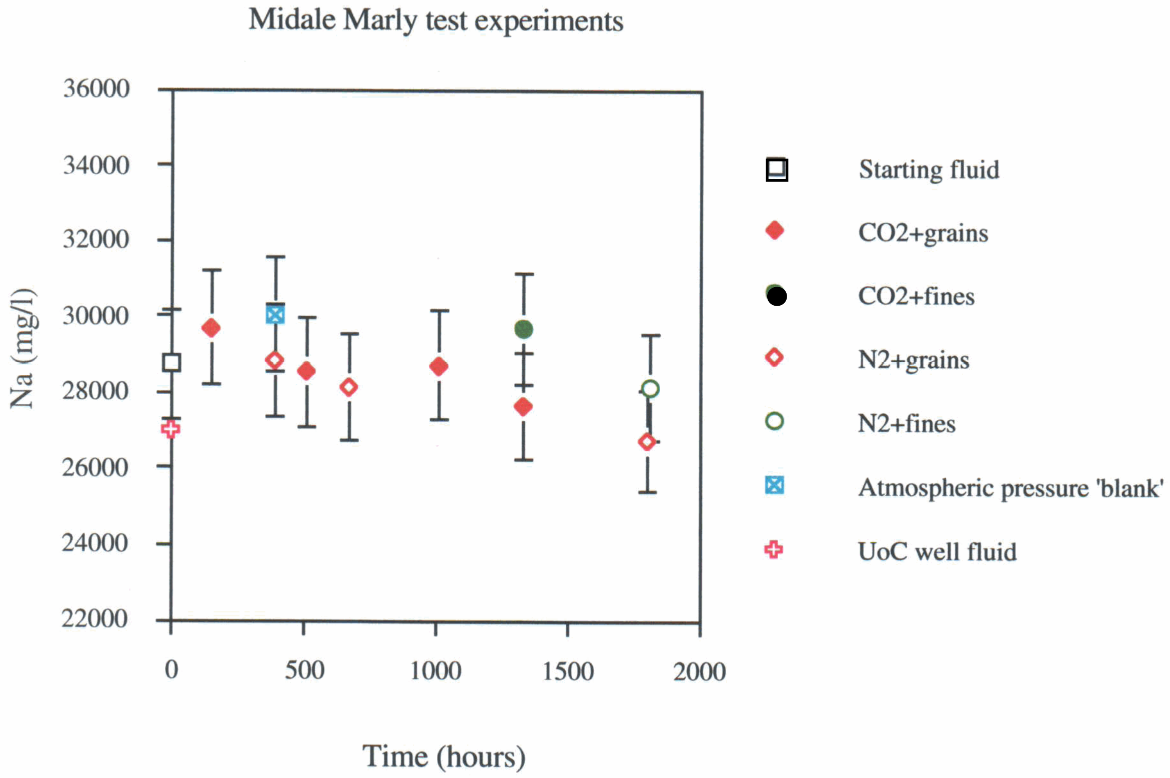

Figure 2 Variation of measured Mg concentrations over time.

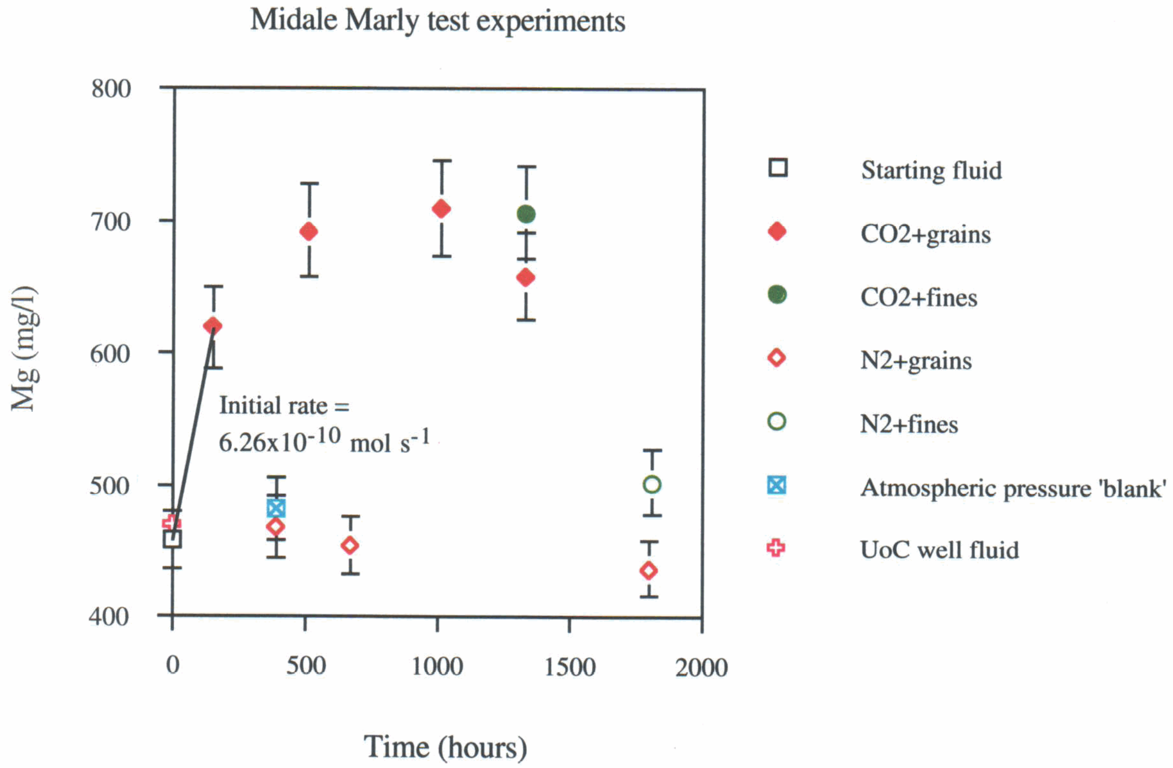

Figure 3 Variation of measured Ca concentrations over time.

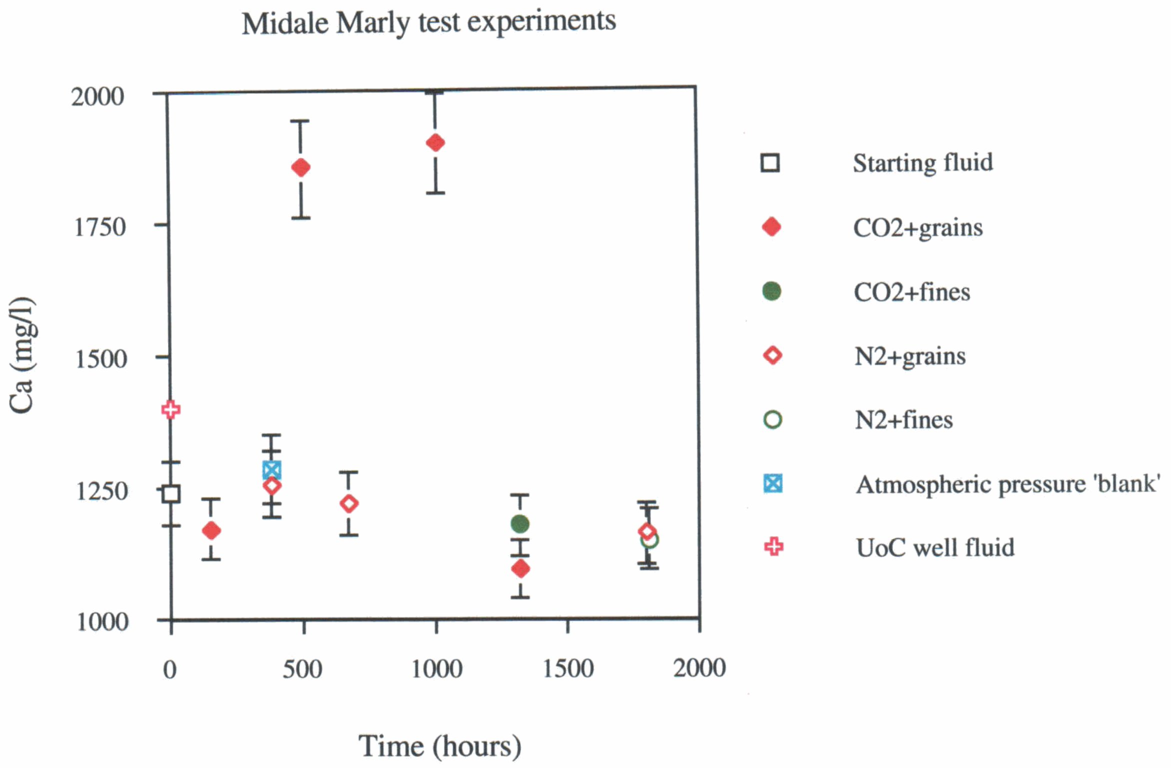

Figure 4 Variation of measured Sr concentrations over time.

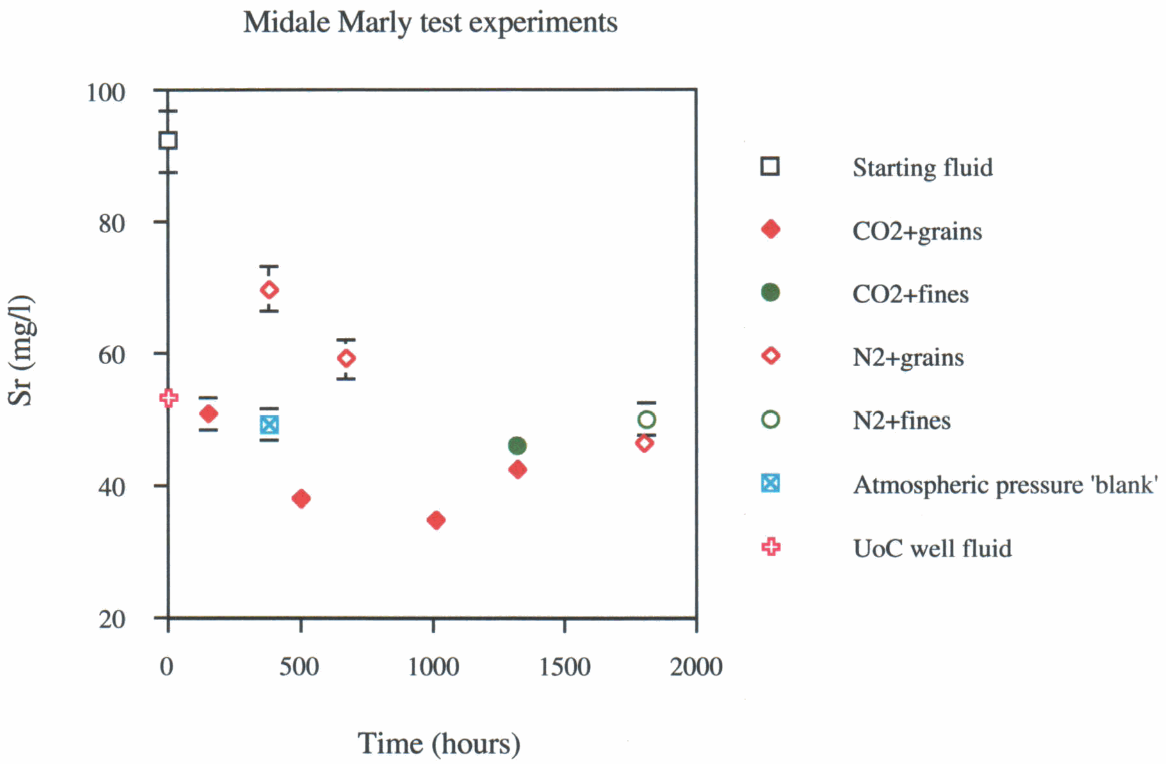

Figure 5 Variation of measured Si concentrations over time.

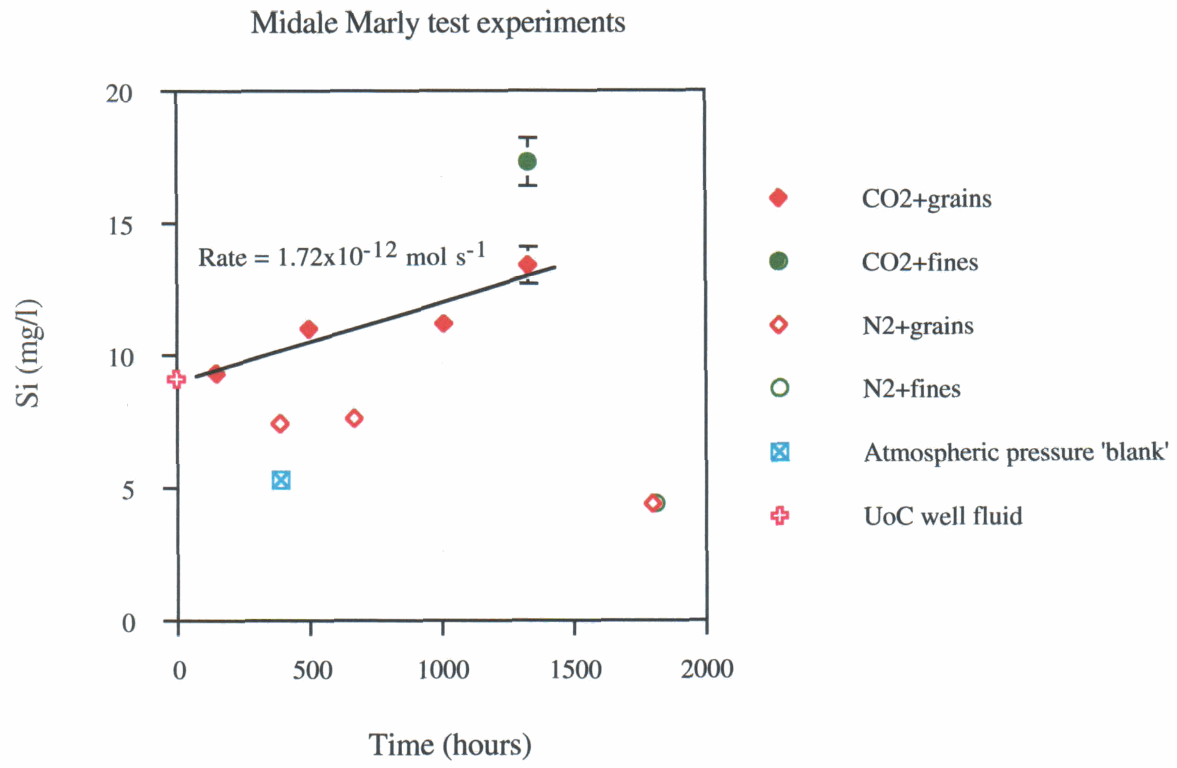

Table 1 Recipe for making up a synthetic equivalent of the porewater from well b14-13-6-14 for the test experiments.

Test solution

Key information	Borehole	b14-13-6-14
	Latitude	49.47911
	Longitude	103.777
	Fluid chemistry from University of Calgary baseline survey	
	Plug sample id	BGS2A
	MPG code	H636
	Plug sample horizo	M2
	Perf horiz	M evaporite to M3

Comments

Not a brilliant match between location of perforated horizon (i.e. fluid sample) and location of solid sample.
This information is for the initial 'look see' text experiments.
Synthetic solution predicted to be some 9% richer in Cl compared to University of Calgary analysis.

Information relating to laboratory chemicals used to make up synthetic soultions.

Chemical	Source	Grade	min assay	batch number	mol wt	mol wt info	Date ordered	Notes
LiCl	-	-	-	-	-	-	-	
NaCl	BDH	ARISTAR	99.5	-	58.44	from packet	Old stock	
KCl	Fisher Chemicals	-	99.72	-	74.56	from packet	Old stock	
MgCl2	-	-	-	-	-	-	-	
MgCl2.6H2O	Fisher Chemicals		99.1	-	203.31	from packet	Old stock	
CaCl2	-	-	-	-	-	-	-	
CaCl2.2H2O	BDH	AnalaR	99.5	-	147.02	from packet	Old stock	
SrCl2	-	-	-	-	-	-	Old stock	
SrCl2.6H2O	BDH	AnalaR	98.5	-	266.62	from packet	Very old stock	
NaHCO3	BDH	AnalaR	99.5	-	84.01	from packet	Old stock	
H2SO4 (conc)	BDH	ARISTAR	98.0	-	98.07	from packet	Old stock	
Si (1000ppm sln)	BDH	-	-	-	-	-	Old stock	In solution with HF
NaOH	BDH	ARISTAR	98.0	-	40.00	from packet	Old stock	

Original Uni. of Calgary analysis

Location	**b14-13-6-14**	Equivalent mol/l	Comments
Temp (oC)	22.3		
pH	6.62		
Alk (mg/L)	422.0	6.9058E-03	
S^{2-} (ppm)	52.8	1.6469E-03	Omit - not studying redox
Na (mg/L)	27040	1.1762E+00	
K (mg/L)	294.4	7.5294E-03	
Ca (mg/L)	1399	3.4905E-02	
Mg (mg/L)	471.0	1.9375E-02	
Mn (mg/L)	0.94	1.7110E-05	Omit - minor
Li (mg/L)	10.47	1.5086E-03	Omit - from drilling fluid?
Fe (mg/L)	1.077	1.9284E-05	Omit - not studying redox
Sr (mg/L)	53.06	6.0557E-04	
Ba (mg/L)	0.281	2.0460E-06	Omit - minor
Si (mg/L)	9.15	3.2574E-04	
Cl (mg/L)	39440	1.1126E+00	
SO_4 (mg/L)	3460	3.6019E-02	
Acetate (mg/L)		-	
Propionic (mg/L)		-	

	For analytes on left, amount to add (wt in g, ml for Si sln)				
	Ingredient	for 1 litre	for 2 litres	for 4 litres	for 8 litres
Component solution 1	NaHCO3	0.5802	1.1603	2.3206	4.6413
	-	-	-	-	-
	NaCl	64.1215	128.2430	256.4860	512.9720
	KCl	0.5614	1.1228	2.2456	4.4911
	CaCl2.2H2O	5.1318	10.2635	20.5270	41.0541
	MgCl2.6H2O	3.9391	7.8782	15.7563	31.5126
	-	-	-	-	-
	-	-	-	-	-
	-	-	-	-	-
	SrCl2.6H2O	0.1615	0.3229	0.6458	1.2917
	-	-	-	-	-
Component solution 2	Si std sln	9.1500	18.3000	36.6000	73.2000
	From above chlorides - so this element to vary from measured values				
	conc H2SO4	3.5324	7.0648	14.1296	28.2592
	-	-	-	-	-
	-	-	-	-	-
	Extras				
	NaOH	2.8815	5.7631	11.5261	23.0523

Table 2 Details of the individual Midale Marly test experiments conducted during this study.

HTL run no.	Run conditions	Type	On	Off	Duration (hours)	Approx. duration (weeks)
1031	60°C, 160 bar	CO_2, 250-500μm	19/6/02 12:25	24/6/02 15:00	122.58	1
1026	60°C, 160 bar	CO_2, 250-500μm	1/5/02 10:30	22/5/02 10:45	504.25	3
1025	60°C, 160 bar	CO_2, 250-500μm	1/5/02 10:30	12/6/02 11:30	1009.00	6
1024	60°C, 160 bar	CO_2, 250-500μm	1/5/02 10:30	25/6/02 16:45	1326.25	8
1023	60°C, 160 bar	CO_2, <250μm	1/5/02 10:30	25/6/02 17:15	1326.75	8
1027	60°C, room pressure	N_2, 250-500μm	27/5/02 10:15	12/6/02 12:00	385.75	3
1033	60°C, 160 bar	N_2, 250-500μm	19/6/02 16:00	17/7/02 14:10	670.17	4
1032	60°C, 160 bar	N_2, 250-500μm	19/6/02 14:00	5/7/02 15:20	385.33	6
1028	60°C, 160 bar	N_2, 250-500μm	23/5/02 10:15	6/8/02 11:30	1801.25	8
1030	60°C, 160 bar	N_2, <250μm	23/5/02 10:15	6/8/02 10:20	1800.08	8

HTL run no.	Solid weight (grammes)	Fluid weight (grammes)	Lab pH #	pH shown in Apdx 1	LIMS code reference in Apdx 1
1031	5.0002	49.9992	7.10	7.82	10378-0014
1026	5.0003	49.9984	6.20	7.65	10378-0002
1025	5.002	50.0033	6.23	7.56	10378-0001
1024	5.002	49.995	6.40	7.77	10378-0013
1023	4.9995	50.0179	6.34	7.69	10378-0012
1027	5.0007	49.9995	7.83	6.79	10378-0003
1033	5.004	49.9998	7.23	7.47	10378-0007
1032	5.0007	50.0004	7.08	7.30	10378-0006
1028	5.0004	50.0003	8.11	6.88	10378-0004
1030	5.0000	49.9994	8.07	7.06	10378-0005

\# This is the recommended pH value to use, and it was taken immediately after sampling. Note that this pH value is that taken at atmospheric pressure after sample depressurisation. The one reported in the analytical data in Appendix 1 is that taken some time (days/weeks) after sampling.

Table 3 Analytes, detection limits and estimated uncertainties (for the dilutions used).

Analyte	Instrument detection limits ($mg\ l^{-1}$) #	Effective detection limits #		Uncertainty †
		$mg\ l^{-1}$	$mol\ l^{-1}$	(± %)
Li	0.025	1.25	1.8×10^{-4}	NA
Na	0.35	17.5	7.6×10^{-4}	<5
K	0.5	25	6.4×10^{-4}	<5
Mg	0.01	0.5	2.1×10^{-5}	<5
Ca	0.1	5	1.2×10^{-4}	<5
Sr	0.002	0.1	1.1×10^{-6}	<5
Ba	0.002	0.1	7.3×10^{-7}	>10
V	0.01	0.5	9.8×10^{-6}	NA
Cr	0.002	0.1	1.9×10^{-6}	NA
Mn	0.002	0.1	1.8×10^{-6}	>10
Total Fe	0.01	0.5	9.0×10^{-6}	>10
Co	0.002	0.1	1.7×10^{-6}	NA
Ni	0.001	0.05	8.5×10^{-7}	>10
Cu	0.002	0.1	1.6×10^{-6}	>10
Zn	0.005	0.25	3.8×10^{-6}	>10
Mo	0.015	0.75	7.8×10^{-6}	NA
Cd	0.002	0.1	8.9×10^{-7}	NA
Pb	0.005	0.25	1.2×10^{-6}	NA
Al	0.01	0.1 *	3.7×10^{-6} *	5-10
As	0.015	0.75	1.0×10^{-5}	NA
Se	0.015	0.75	9.5×10^{-6}	NA
B	0.01	0.5	4.6×10^{-5}	NA
Total P	0.01	0.5	1.6×10^{-5}	>10
Total S	0.25	1.25	3.9×10^{-5}	<5
Si	0.075	3.75	1.3×10^{-4}	5-10
SiO_2	0.16	8	1.3×10^{-4}	5-10
F^-	0.05	2.5	1.3×10^{-4}	>10
Cl^-	0.1	5	1.4×10^{-4}	<5
Br^-	0.03	1.5	1.9×10^{-5}	NA
NO_2^-	0.01	0.5	1.1×10^{-5}	NA
NO_3^-	0.04	2	3.2×10^{-5}	NA
SO_4^{2-}	0.3	15	1.6×10^{-4}	<5
HCO_3^-	22	22	3.6×10^{-4}	<5 to >10 §
CO_3^{2-}	22	22	3.7×10^{-4}	<5 to >10 §
TIC	1	20	1.7×10^{-3}	<5 to >10 §
TOC	1	20	1.7×10^{-3}	<5 to >10 §

Limits of quantification depend on how much dilution is needed to bring solutions with high concentrations of total dissolved solids down to reasonable levels. Dilution causes an effective worsening of the detection limits. During this study, samples were diluted 20x or 50x prior to analysis (see text).

† Illustrative uncertainties considered 'typical' for the concentration ranges likely to be found in this study. In general, concentrations <10x the detection limit have uncertainties in the order of ≥10%, concentrations >10x the detection limit have uncertainties in the order of ≤5% etc.

NA Not applicable, as element was below the detection limit.

* Lower than usual detection limits achieved by *manually* checking the original ICP traces and searching for the presence (or not) of a 'real' signal.

§ Results dependent upon the specific sample being considered.

Appendix 1

Primary fluid chemical analytical data
(electronic scans of original documents)

Note that most (but not all) of the data presented in this appendix are relevant to the initial text experiments. Any additional data in this appendix will be described in later reports.

Note that for pH, the values in Table 2 above should be used and not the values in this appendix.
Note also that the starting fluid used in the initial test batch experiments is called "Weyburn test fluid" in this appendix and that this had an initial pH of 8.29 when first prepared.

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ANALYTICAL GEOCHEMISTRY LABORATORIES
ANALYSIS REPORT COVER NOTE

This report consists of a 1 page Analysis Report Cover Note and 4 pages of test data

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Report Number:	10378/10	Customer Ref/Order No:	IR 00739
Report Date:	31 October 2002	Sample(s) received on:	19 August 2002
Issue Status:	Complete	Analysis commenced on:	22 August 2002

Sample Details

All samples were received in good condition.

Analysis Details

Determinands	Test Method	Procedure	Notes
Ca, Mg, Na, total P, total S, Si, Ba, Sr, Mn, total Fe, Al, Ni, Cu, Zn, Cr, Mo, Cd, Pb, V, Li, As, Se	ICP-AES	AGN 2.3.5	
K, Co, B	ICP-AES		N
Cl, SO_4, NO_3, NO_2, Br, F	Ion chromatography	AGN 2.3.6	
pH and alkalinity	Potentiometric titration	AGN 2.3.7	
TOC, TIC	TOC analyser	AGN 2.3.8	

Tests marked N in the above table are not included in the UKAS Accreditation Schedule for this Laboratory.

There may be a negative bias of up to 10% for Co data reported by ICP-AES. The element has been temporarily withdrawn from the scope of accreditation pending investigation into this anomaly.

Most ionic charge balances are within the normally acceptable 5% limits; all are within 6%. This is considered acceptable for such high salinity samples.

Because of limitations with the current software used for reporting data, the number of significant figures quoted in the attached table may not be representative of the actual uncertainty. Data should be considered accurate to no more than three significant figures.

This report is issued under complete status. All analyses requested have been completed and results are issued with full compliance of data verification.

Report authorised by: .... Date: ....31/10/02....

Mr S Reeder
Aqueous Analytical Section Manager

Report Number: 10378/10

British Geological Survey
ANALYSIS REPORT

31/10/2002

LIMS Code	Sample Code	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{-}	Cl^{-}	SO_4^{2-}	NO_3^{-}	Cation Total	Anion Total
			mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	meq l^{-1}	meq l^{-1}
10378-0001	Run 1025	7.56	1898	710	28707	330	1886	44293	2692	<2.00	1411.55	1336.46
10378-0002	Run 1026	7.65	1853	693	28535	331	1748	46613	3825	<2.00	1400.08	1423.24
10378-0003	Run 1027	6.79	1286	482	30020	339	<22	49909	2335	<2.00	1419.54	1456.94
10378-0004	Run 1028	6.88	1164	437	26725	312	25	45727	2065	<2.00	1265.63	1333.73
10378-0005	Run 1030	7.06	1151	503	28096	333	24	49647	2046	<2.00	1330.72	1443.98
10378-0006	Run 1032	7.30	1256	468	28821	330	50	42184	2205	<2.00	1365.06	1237.18
10378-0007	Run 1033	7.47	1221	454	28098	320	79	48704	2209	<2.00	1330.10	1421.68
10378-0008	Run 1038	7.08	1276	529	25934	492	37	46724	2651	<2.00	1248.53	1373.88
10378-0009	B14-13-6-14	7.74	1241	429	25381	295	340	45724	2661	<2.00	1209.38	1350.85
10378-0010	d8-23-6-14	7.64	1247	515	25370	468	212	46566	2458	<2.00	1220.68	1368.28
10378-0011	Weyburn test fluid	7.69	1140	425	25802	301	122	38742	1695	<2.00	1226.51	1130.76
10378-0012	Run 1023/1	7.69	1178	707	29646	341	934	45716	4124	<2.00	1416.35	1390.82
10378-0013	Run 1024/1	7.77	1097	659	27634	355	928	49842	2065	<2.00	1321.10	1464.43
10378-0014	Run 1031/1	7.82	1172	620	29690	338	424	49383	2100	<2.00	1410.89	1444.13

LIMS Code	Sample Code	Balance	Br^-	NO_2^-	F^-	TOC	TIC	Total P	Total S	Si	SiO_2	Ba
		%	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}
10378-0001	Run 1025	2.73	<1.50	<0.50	<2.50	252	148	0.517	960	11.2	23.87	<0.100
10378-0002	Run 1026	-0.82	<1.50	<0.50	<2.50	255	181	<0.500	951	11.0	23.46	0.104
10378-0003	Run 1027	-1.30	<1.50	<0.50	7.46	<20.0	<10.0	<0.500	1000	5.30	11.34	<0.100
10378-0004	Run 1028	-2.62	<1.50	<0.50	7.06	60.9	<10.0	0.850	903	4.43	9.48	0.142
10378-0005	Run 1030	-4.08	<1.50	<0.50	8.54	83.5	<10.0	<0.500	954	4.42	9.45	0.127
10378-0006	Run 1032	4.91	<1.50	<0.50	8.63	27.9	<10.0	0.611	976	7.38	15.80	0.140
10378-0007	Run 1033	-3.33	<1.50	<0.50	8.69	<20.0	13.5	0.606	936	7.65	16.36	0.111
10378-0008	Run 1038	-4.78	<1.50	<0.50	<2.50	<20.0	<10.0	0.745	1043	14.0	29.95	0.196
10378-0009	B14-13-6-14	-5.53	<1.50	<0.50	<2.50	<20.0	63.8	<0.500	1042	8.23	17.61	<0.100
10378-0010	d8-23-6-14	-5.70	<1.50	<0.50	<2.50	<20.0	35.2	<0.500	1014	11.8	25.24	<0.100
10378-0011	Weyburn test fluid	4.06	<1.50	<0.50	10.70	<20.0	21.9	<0.500	931	4.61	9.85	<0.100
10378-0012	Run 1023/1	0.91	<1.50	<0.50	<2.50	341	134	0.550	967	17.3	37.05	<0.100
10378-0013	Run 1024/1	-5.15	<1.50	<0.50	3.50	205	133	<0.500	915	13.4	28.67	<0.100
10378-0014	Run 1031/1	-1.16	<1.50	<0.50	6.88	92.0	71.9	<0.500	982	9.33	19.96	<0.100

LIMS Code	Sample Code	Sr	Mn	Total Fe	Al	Co	Ni	Cu	Zn	Cr	Mo	Cd
		mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}
10378-0001	Run 1025	34.9	0.305	7.00	1.42	<0.100	0.443	0.381	0.260	<0.100	<0.750	<0.100
10378-0002	Run 1026	38.0	0.238	0.741	1.39	<0.100	0.298	0.412	0.250	<0.100	<0.750	<0.100
10378-0003	Run 1027	49.2	<0.100	1.27	0.503	<0.100	<0.050	0.166	<0.250	<0.100	<0.750	<0.100
10378-0004	Run 1028	46.4	<0.100	1.22	0.668	<0.100	<0.050	0.234	<0.250	<0.100	<0.750	<0.100
10378-0005	Run 1030	49.9	<0.100	0.994	0.586	<0.100	0.134	0.220	<0.250	<0.100	<0.750	<0.100
10378-0006	Run 1032	69.8	<0.100	2.69	0.479	<0.100	0.120	0.223	<0.250	<0.100	<0.750	<0.100
10378-0007	Run 1033	59.1	<0.100	0.734	1.16	<0.100	0.143	0.507	1.19	<0.100	<0.750	<0.100
10378-0008	Run 1038	25.0	<0.100	0.755	2.87	<0.100	0.421	0.352	<0.250	<0.100	<0.750	<0.100
10378-0009	B14-13-6-14	25.3	<0.100	0.607	0.536	<0.100	<0.050	0.147	<0.250	<0.100	<0.750	<0.100
10378-0010	d8-23-6-14	19.8	<0.100	1.110	0.590	<0.100	<0.050	<0.100	<0.250	<0.100	<0.750	<0.100
10378-0011	Weyburn test fluid	197	<0.100	0.631	0.796	<0.100	<0.050	0.217	<0.250	<0.100	<0.750	<0.100
10378-0012	Run 1023/1	46.1	<0.100	0.554	0.509	<0.100	1.36	0.125	<0.250	<0.100	<0.750	<0.100
10378-0013	Run 1024/1	42.6	<0.100	<0.500	0.152	<0.100	0.092	<0.100	<0.250	<0.100	<0.750	<0.100
10378-0014	Run 1031/1	50.8	<0.100	0.607	0.297	<0.100	0.162	0.149	<0.250	<0.100	<0.750	<0.100

LIMS Code	Sample Code	Pb	V	Li	B	As	Se
		mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}	mg l^{-1}
10378-0001	Run 1025	<0.250	<0.500	<1.25	<0.50	<0.750	<0.750
10378-0002	Run 1026	<0.250	<0.500	<1.25	<0.50	<0.750	<0.750
10378-0003	Run 1027	<0.250	<0.500	<1.25	<0.50	<0.750	<0.750
10378-0004	Run 1028	<0.250	<0.500	<1.25	<0.50	<0.750	<0.750
10378-0005	Run 1030	<0.250	<0.500	<1.25	<0.50	<0.750	<0.750
10378-0006	Run 1032	<0.250	<0.500	<1.25	<0.50	<0.750	<0.750
10378-0007	Run 1033	<0.250	<0.500	<1.25	<0.50	<0.750	<0.750
10378-0008	Run 1038	<0.250	<0.500	<1.25	<0.50	<0.750	<0.750
10378-0009	B14-13-6-14	<0.250	<0.500	<1.25	<0.50	<0.750	<0.750
10378-0010	d8-23-6-14	<0.250	<0.500	<1.25	<0.50	<0.750	<0.750
10378-0011	Weyburn test fluid	<0.250	<0.500	<1.25	<0.50	<0.750	<0.750
10378-0012	Run 1023/1	<0.250	<0.500	<1.25	<0.50	<0.750	<0.750
10378-0013	Run 1024/1	<0.250	<0.500	<1.25	<0.50	<0.750	<0.750
10378-0014	Run 1031/1	<0.250	<0.500	<1.25	<0.50	<0.750	<0.750

Appendix 2

Formatted analytical data for just the Midale Marly experiments that are used in this report.

Note that data in brackets () are identified as 'suspect' in some way, and may well have not been used in some of the figures in this report.

ID number	Gas	State	Pressure (MPa)	Temp. (°C)	Run no.	On	Off	Elapse time (h)	Solid used (g)	Solution used (g)
BGS2A	-	Test fluid (initial analysis)						0.0	-	-
(HTL 134)	-	Test fluid (later analysis)						0.0	-	-
(Marly)	-	Test fluid (final repeat analysis)						0.0	-	-
	CO2	250-500μm	16.0	60	1031	6/19/02 12:25	6/25/02 16:15	147.8	5.0002	49.9992
	CO2	250-500μm	16.0	60	1026	5/1/02 10:30	5/22/02 10:45	504.2	5.0003	49.9984
	CO2	250-500μm	16.0	60	1025	5/1/02 10:30	6/12/02 11:30	1009.0	5.002	50.0033
	CO2	250-500μm	16.0	60	1024	5/1/02 10:30	6/25/02 16:45	1326.2	5.002	49.995
	Air	250-500μm	Atmospheric	60	1027	5/27/02 10:15	6/12/02 12:00	385.7	5.0007	49.9995
	N2	250-500μm	16.0	60	1033	6/19/02 16:00	7/17/02 14:10	670.2	5.004	49.9998
	N2	250-500μm	16.0	60	1032	6/19/02 14:00	7/5/02 15:20	385.3	5.0007	50.0004
	N2	250-500μm	16.0	60	1028	5/23/02 10:15	8/6/02 11:30	1801.2	5.0004	50.0003
	CO2	<250 μm	16.0	60	1023	5/1/02 10:30	6/25/02 17:15	1326.8	4.9995	50.0179
	N2	<250 μm	16.0	60	1030	5/23/02 10:15	8/6/02 22:20	1812.1	5.0000	49.9994

n/d = not determined
n/s = no sample
( ) = uncertain data
< = value less than detection limit

Comments	LIMS code	pH	Ca2+ mg l-1	Mg2+ mg l-1	Na+ mg l-1	K+ mg l-1	HCO3- (old) mg l-1	HCO3- (new) mg l-1
	10378-0011	8.29	1140	425	25802	301	122	n/d
	10583-0021	7.52	(1074)	(387)	25522	312	<88.0	n/d
	10762-0040	7.74	1240	458	28744	360	n/d	54
	10378-0014	7.10	(1172)	620	29690	338	(424)	n/d
Fe staining on teflon pot and filter assembly	10378-0002	6.20	1853	693	28535	331	(1748)	n/d
Threads on vessel locked. Solid had to be washed through pressure ports in vessel lid	10378-0001	6.23	1898	710	28707	330	(1886)	n/d
See 'rusty-coloured' staining	10378-0013	6.40	(1097)	659	27634	355	(928)	n/d
Not at pressure throughout expt.	10378-0003	7.83	1286	482	30020	339	<22.0	n/d
	10378-0007	7.23	1221	454	28098	320	78.8	n/d
Fluid cloudy when sampled.	10378-0006	7.08	1256	468	28821	330	49.5	n/d
	10378-0004	8.11	1164	437	26725	312	24.9	n/d
See very slight pinky/rusty staining	10378-0012	6.34	(1178)	707	29646	341	(934)	n/d
	10378-0005	8.07	1151	503	28096	333	24.1	n/d

Cl- mg l-1	SO42- mg l-1	NO3- mg l-1	Cation Total meq l-1	Anion Total meq l-1	Balance %	Br- mg l-1	NO2- mg l-1	HPO42- mg l-1	F- mg l-1	TOC mg l-1	TIC mg l-1	Total P mg l-1	Total S mg l-1
38742	1695	<2.00	1227	1131	4.06	<1.50	<0.50	n/d	10.7	<20.0	21.9	<0.50	931
44759	2370	25.5	1206	1313	-4.25	<15.0	<10.0	<50.0	6.76	<48.0	<24.0	<1.0	(820)
46589	2467	89.6	1361	1368	-0.24	<10.0	<5.0	<50.0	<5.0	n/d	n/d	<1.0	941
49383	2100	<2.00	1411	1444	-1.16	<1.50	<0.50	n/d	6.88	92.0	71.9	<0.50	982
46613	3825	<2.00	1400	1423	-0.82	<1.50	<0.50	n/d	<2.50	255	181	<0.50	951
44293	2692	<2.00	1412	1336	2.73	<1.50	<0.50	n/d	<2.50	252	148	0.517	960
49842	2065	<2.00	1321	1464	-5.15	<1.50	<0.50	n/d	3.50	205	133	<0.50	915
49909	2335	<2.00	1420	1457	-1.30	<1.50	<0.50	n/d	7.46	<20.0	<10.0	<0.50	1000
48704	2209	<2.00	1330	1422	-3.33	<1.50	<0.50	n/d	8.69	<20.0	13.5	0.606	936
42184	2205	<2.00	1365	1237	4.91	<1.50	<0.50	n/d	8.63	27.9	<10.0	0.611	976
45727	2065	<2.00	1266	1334	-2.62	<1.50	<0.50	n/d	7.06	60.9	<10.0	0.850	903
45716	4124	<2.00	1416	1391	0.91	<1.50	<0.50	n/d	<2.50	341	134	0.550	967
49647	2046	<2.00	1331	1444	-4.08	<1.50	<0.50	n/d	8.54	83.5	<10.0	<0.50	954

Si mg l-1	SiO2 mg l-1	Ba mg l-1	Sr mg l-1	Mn mg l-1	Total Fe mg l-1	Al mg l-1	Co mg l-1	Ni mg l-1	Cu mg l-1	Zn mg l-1	Cr mg l-1	Mo mg l-1	Cd mg l-1
4.61	9.85	<0.10	(197)	<0.10	0.631	0.796	<0.10	<0.050	0.217	<0.25	<0.10	<0.75	<0.10
<7.50	<16.0	<0.20	94.7	<0.20	<1.0	<1.0	<0.20	<0.10	<0.20	<0.50	<0.20	<1.50	<0.20
<7.50	<16.0	<0.20	92.3	<0.20	<1.0	<1.0	<0.20	<0.10	0.439	<0.50	<0.20	<1.50	<0.20
9.33	20.0	<0.10	50.8	<0.10	0.607	0.297	<0.10	0.162	0.149	<0.25	<0.10	<0.75	<0.10
11.0	23.5	0.104	38.0	0.238	0.741	1.39	<0.10	0.298	0.412	0.250	<0.10	<0.75	<0.10
11.2	23.9	<0.10	34.9	0.305	7.00	1.42	<0.10	0.443	0.381	0.260	<0.10	<0.75	<0.10
13.4	28.7	<0.10	42.6	<0.10	<0.50	0.152	<0.10	0.0920	<0.10	<0.25	<0.10	<0.75	<0.10
5.30	11.3	<0.10	49.2	<0.10	1.27	0.503	<0.10	<0.05	0.166	<0.25	<0.10	<0.75	<0.10
7.65	16.4	0.111	59.1	<0.10	0.734	1.16	<0.10	0.143	0.507	1.19	<0.10	<0.75	<0.10
7.38	15.8	0.140	69.8	<0.10	2.69	0.479	<0.10	0.120	0.223	<0.25	<0.10	<0.75	<0.10
4.43	9.48	0.142	46.4	<0.10	1.22	0.668	<0.10	<0.05	0.234	<0.25	<0.10	<0.75	<0.10
17.3	37.1	<0.10	46.1	<0.10	0.554	0.509	<0.10	1.36	0.125	<0.25	<0.10	<0.75	<0.10
4.42	9.45	0.127	49.9	<0.10	0.994	0.586	<0.10	0.134	0.220	<0.25	<0.10	<0.75	<0.10

Pb mg l-1	V mg l-1	Li mg l-1	B mg l-1	As mg l-1	Se mg l-1
<0.25	<0.50	<1.25	<0.50	<0.75	<0.75
<0.50	<1.00	<2.50	<2.50	<1.50	<1.50
<0.50	<1.00	<2.50	<2.50	<1.50	<1.50
<0.25	<0.50	<1.25	<0.50	<0.75	<0.75
<0.25	<0.50	<1.25	<0.50	<0.75	<0.75
<0.25	<0.50	<1.25	<0.50	<0.75	<0.75
<0.25	<0.50	<1.25	<0.50	<0.75	<0.75
<0.25	<0.50	<1.25	<0.50	<0.75	<0.75
<0.25	<0.50	<1.25	<0.50	<0.75	<0.75
<0.25	<0.50	<1.25	<0.50	<0.75	<0.75
<0.25	<0.50	<1.25	<0.50	<0.75	<0.75
<0.25	<0.50	<1.25	<0.50	<0.75	<0.75
<0.25	<0.50	<1.25	<0.50	<0.75	<0.75