

APPLICATION OF FLUID-ROCK REACTION STUDIES
TO
IN SITU RECOVERY FROM OIL SAND DEPOSITS
ALBERTA, CANADA --- III
ADDITIONAL DATA
ON AN
EXPERIMENTAL-STATISTICAL STUDY
OF
WATER-BITUMEN-SHALE REACTIONS

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ABSTRACT

This Open File Report makes available additional geochemical and other data to supplement that reported by the authors in two papers, with the same general title, published in the February, 1983 issue of *Geochimica et Cosmochimica Acta*.

With respect to the starting materials, differences between duplicate analyses of trace elements in the bitumen emphasize the tremendous difficulty in cleaning bitumen prior to analysis. A complete grain size distribution for the shale is provided without further comment.

For sixteen experiments in the complete set of 96, the bitumen was separated into four fractions (saturates, aromatics, resins and asphalt- enes) following the hydrothermal treatment. Although there are differ- ences in composition between the subsets shale and no-shale, as well as between the sixteen bitumens and the starting bitumen, their magnitude is insufficient to indicate that the experimental conditions were severe enough to induce major changes in the composition of the bitumen.

The composition of the colloidal material found in most of the experi- ments with shale has been calculated in terms of oxides, and for many of the twelve analyses reported, the Al:Si ratios fall in a fairly narrow range, even though the total amount of colloidal material present varies widely. This is interpreted in terms of a common mineral com- ponent in suspension in these cases.

An annotated ANOVA is presented in the Appendix for the individual element concentrations for the experiments with shale.

Of the 24 experiments which effectively represent "blank" runs to test contamination effects of the autoclaves, only those eight of 92 hours duration were carried out, some in triplicate to test autoclaves of

different materials. The chemical composition of the aqueous phase is given for sixteen of these "blank" runs and with the exception of Cr it can be stated that contamination from the autoclaves is effectively negligible.

The final set of data reported are the aqueous phase compositions from the 24 experiments designed to test the effects of pH, temperature, time and salinity on the removal of trace elements from bitumen. The most dramatic effect is the reduction in pH to the range 2.5 to 3.2 for those experiments in which pH was not controlled by the addition of borax. Increased sulphate at higher pH values may be due to hydrolytic desulphurization reaction of the sulphonic acid group of the bitumen.

INTRODUCTION

Boon and Hitchon (1983a, b) carried out a factorial experiment in which a shale from the Lower Cretaceous McMurray Formation in the Athabasca oil sand deposit of Alberta, in the presence or absence of bitumen, was subjected to hydrothermal treatment with aqueous fluids of varying pH and salinity, at two different temperatures (200°C and 250°C), for periods of 20, 44 and 92 hours. The aqueous fluid was analyzed, and the analytical data subjected to statistical factor analysis and analysis of variance. Solution mineral equilibria were calculated for the aqueous phase and x-ray diffractograms obtained for the separated solids. Data representing the departures from equilibrium, and normalized x-ray diffraction peak intensities, were studied by statistical analysis of variance. The reactions which took place simulated conditions during in situ steam injection and were related by these authors to practical in situ recovery operations. The interested reader is referred to these papers for complete details.

The factorial experiment comprised six experimental variables, and the complete set of 96 separate experiments is shown diagrammatically in Figure 1. Boon and Hitchon (1983a, b) reported the results of experiments 1 to 48, that is, those with shale present (shown screened in Figure 1). We report here the results of experiment 49 to 96, without shale present; experiments 49 to 72 effectively represent "blank" runs to test contamination effects from the autoclaves, and experiments 73 to 96 represent runs to examine the effects of pH, temperature, time and salinity on the removal of trace elements from bitumen. Figure 1 also shows the experiment identification code that is used in those tables in this Open File Report which include analytical or statistical data. For example, experiment No. 96, without shale, in which bitumen was reacted with controlled salinity and pH, at 250°C for 92 hours, has the identification code _ BbT92SW. In addition to reporting the results of experiments 49 to 96, we also provide further information on the bitumen

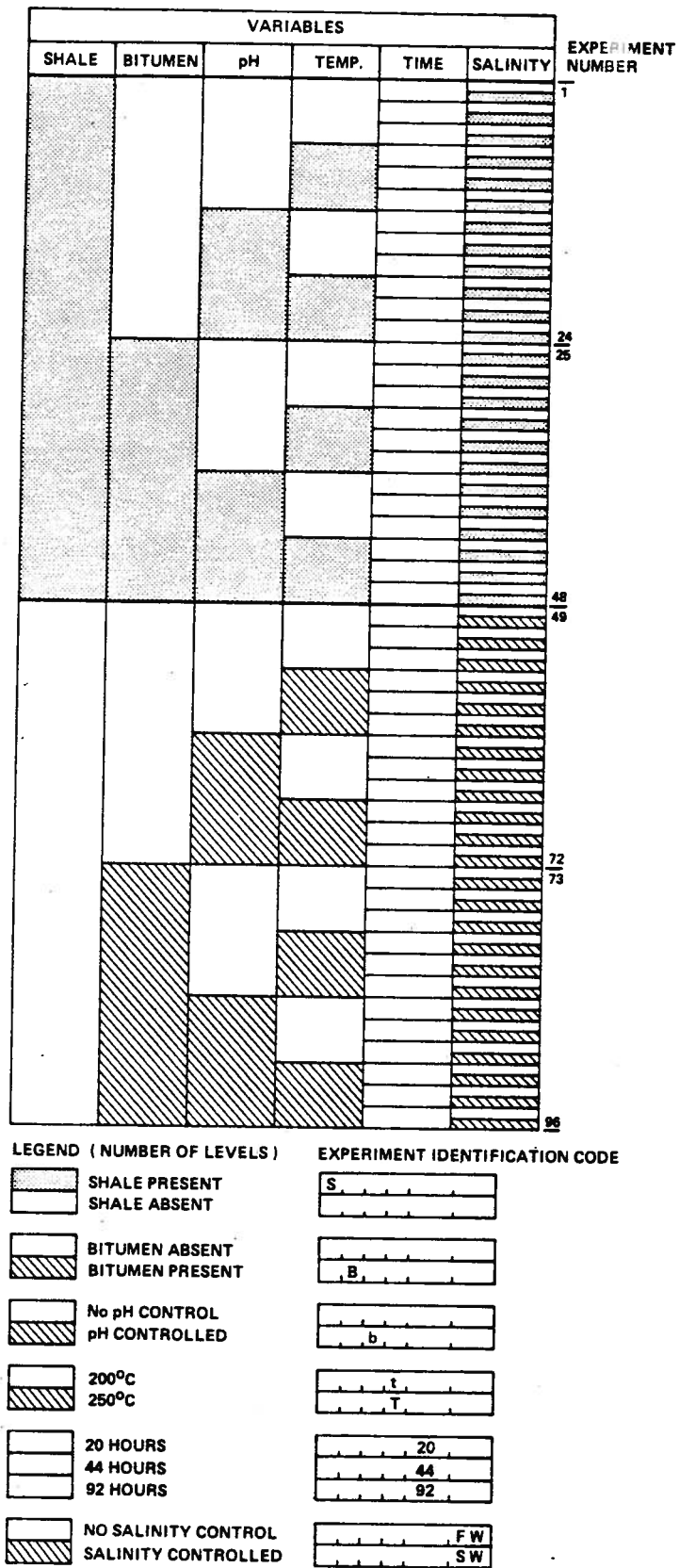


Figure 1. Diagrammatic representation of the factorial experimental design for six variables.

and shale starting materials, the bitumen composition following hydrothermal treatment, the composition of the colloidal phase from the experiments with shale, and an annotated ANOVA for individual element concentrations from these same 48 experiments.

ADDITIONAL DATA ON THE STARTING MATERIALS

BITUMEN

Boon and Hitchon (1983a, Table 3) reported the elemental composition and trace element content of the bitumen; the latter compositional data were the average of two separate determinations which are here shown in Table 1. With the exception of K, the trace element contents in the second analysis are consistently higher than those in the first analysis (see "ratio" column). This difference could reflect either a non-homogeneous distribution of the elements or possibly entrained mineral matter. In their study on trace elements in Alberta crude oils, which included two samples of bitumen from the Athabasca oil sand deposit, Hitchon and Filby (1983) have suggested, based on a subjective estimate, that entrained formation water, fine-grained clay minerals and fine-grained pyrite may each result in contamination of the bitumen by different elements; Na, Rb and Cs in the case of formation water, Ga, Sc and Eu (also Al) from clay minerals, and Fe, Co, Mn, and possibly Cr, from pyrite. From the data in Table 1, only Cr, and possibly P, may be due to contamination, based on much higher ratios. The trace element contents reported here, and by Hitchon and Filby (1983), emphasize the tremendous difficulty in cleaning bitumen prior to analysis, and neither sets of data are really representative of the true trace element content of the bitumen.

The fractions present in this bitumen are as follows: saturates (14%), aromatics (29%), resins (31%), asphaltenes (24%) and 2% discrepancy due to irreversible adsorption of resins on the alumina separation column.

Table 1. Trace element content of the bitumen used in the experiments

Component	This Study				Subjective Probability of Contamination (Hitchon and Filby, 1983, Table 4)
	First Analysis (ppm)	Second Analysis (ppm)	Ratio	Average* (ppm)	
Al	19	32	1.7	26	-
Ba	ND	ND	-	ND	-
Be	1.25	2.13	1.7	1.7	-
Ca	11	19	1.7	15	-
Cd	ND	ND	-	ND	-
Co	0.69	0.98	1.4	0.8	Very high
Cr	0.35	0.91	2.6	0.6	Intermediate/high
Cu	0.55	0.78	1.4	0.7	-
Fe	18	24	1.3	21	Very high
K	40	30	0.8	35	-
Mg	2.2	3.8	1.7	3	-
Mn	0.5	0.7	1.4	0.6	Very high
Na	11	21	1.9	16	High
Ni	52	87	1.7	70	Low
P	1.2	2.6	2.2	1.9	-
SiO ₂	170	170	1.0	170	-
Sr	0.53	0.81	1.5	0.7	-
Ti	5.6	9.7	1.7	8	-
V	168	226	1.3	197	Low
Zn	1.7	2.4	1.4	2.1	-

ND = Not detected

* As reported by Boon and Hitchon (1983a, Table 3)

SHALE

In addition to data on the chemical and mineralogical composition of the shale (Boon and Hitchon, 1983a, Tables 1 and 2, respectively), the grain size distribution for the $> 44 \mu\text{m}$ size fraction was determined by wet sieving, and for the $< 44 \mu\text{m}$ size fraction using a Sedigraph 5000 Particle Size Analyser (Micrometrics, Norcross, Georgia, USA). The results are given in Table 2, without further comment.

The shale contained 0.08 percent bitumen, as determined by Soxhlet extraction with methylene chloride, with the following composition: saturates (11%), aromatics (30%), resins (26%), asphaltenes (32%) and 1% discrepancy due to irreversible adsorption of resins on the alumina separation column.

ADDITIONAL ANALYTICAL DATA ON THE BITUMENS

Boon and Hitchon (1983a) reported only the composition of the aqueous phase in the 48 experiments with shale present. In eight of these experiments, and an additional eight from the series without shale, samples of the bitumen, following hydrothermal treatment, were analyzed for saturates, aromatics, resins and asphaltenes to determine if significant changes in composition had occurred. These results are reported in Table 3. Gas chromatograms were run on all the saturate fractions, which were virtually identical. Comparison of the average contents of the four fractions in the experiments with shale present with those without shale indicates a small decrease in saturates and resins, and a small increase in aromatics and asphaltenes, although the differences are not significant, thereby suggesting that the shale has not acted as a catalyst, under the experiment conditions, to change the gross composition of the bitumen. When the averages for the sixteen experiments are compared with the composition of the original bitumen, the data show a decrease in the contents of aromatics and resins, and a corresponding

Table 2. Grain size distribution of the shale used in the experiments

Size Range (μm)	Weight Percent	Cumulative Weight Percent	100 Minus Cumulative Weight Percent
176.777 - 125.000	0.1	0.1	100.0
125.000 - 88.388	5.7	5.8	99.9
88.388 - 62.500	10.3	16.1	94.2
62.500 - 44.194	7.4	23.5	83.9
44.194 - 31.250	12.8	36.3	76.5
31.250 - 22.097	0.3	36.6	63.7
22.097 - 15.625	1.9	38.5	63.4
15.625 - 11.049	2.2	40.7	61.5
11.049 - 7.813	1.9	42.6	59.3
7.813 - 5.524	3.2	45.8	57.4
5.524 - 3.906	4.2	50.0	54.2
3.906 - 2.762	4.4	54.4	50.0
2.762 - 1.953	4.8	59.2	45.6
1.953 - 1.381	4.5	63.7	40.8
1.381 - 0.977	3.5	67.2	36.3
0.977 - 0.691	2.9	70.1	32.8
0.691 - 0.488	1.9	72.0	29.9
0.488 - 0.244	2.1	74.1	28.0
< 0.244	25.9	100.0	25.9

Table 3 Composition of bitumen from selected experiments

Experiment Number*	Experiment Identification Code*	Composition of the Bitumen				Percent Recovery
		Saturates (%)	Aromatics (%)	Resins (%)	Asphaltenes (%)	
29	SB t92FW	12	22	30	32	96
30	SB t92SW	15	27	33	23	98
35	SB T92FW	14	26	31	28	99
36	SB T92SW	14	25	31	27	97
41	SBbt92FW	17	29	25	27	98
42	SBbt92SW	14	24	32	26	96
47	SBbt92FW	14	27	29	27	97
48	SBbt92SW	14	23	26	33	96
77	B t92FW	12	25	31	28	96
78	B t92SW	13	25	30	28	96
83	B T92FW	13	25	31	31	100
84	B T92SW	14	29	28	28	99
89	Bbt92FW	14	23	26	28	91
90	Bbt92SW	14	28	27	29	98
95	Bbt92FW	15	26	25	30	96
96	Bbt92SW	14	27	29	27	97
Average		13.9	25.7	29.0	28.3	97
Standard Deviation of Mean		0.3	0.5	0.6	0.6	0.5
Original Bitumen		14	29	31	24	98
Bitumen Extracted from Shale		11	30	26	32	99

* See Fig. 1 for experimental conditions and explanation of experiment identification code.

increase in the content of asphaltenes. Although these differences are larger than those between the subsets (shale and no-shale), their magnitude is insufficient to indicate that the experimental conditions were severe enough to induce major changes in the composition of the bitumen.

COMPOSITION OF COLLOIDAL MATERIAL

In their experiments with shale present, Boon and Hitchon (1983a) identified two types of colloidal material, both of which have the propensity for pore plugging during in situ recovery operations. The composition of this colloidal material was not reported because that paper was concerned essentially with water-rock reactions in which the colloidal material takes no part. Nevertheless, its composition is of interest to those involved in in situ operations and is reported in Table 4 in terms of oxides, as calculated from the concentration decrease caused by acidification, the presence of NaCl, or filtration through 0.1 μ m Millipore filters. Based on the factor analyses (ibid.) it is assumed that the Fe-colloid is not bound to the aluminosilicate particles. For many of the experiments, the Al to Si ratios of the colloidal material fall in a fairly narrow range, even though the total amount present varies widely. This is interpreted in terms of a common mineral component in suspension in these cases.

ANOVA FOR INDIVIDUAL ELEMENT CONCENTRATIONS EXPERIMENTS 1 TO 48

Boon and Hitchon (1983a) treated the aqueous phase results using statistical factor analysis followed by analysis of variance (ANOVA) of the factor scores. By using these methods they were able to reduce a vast amount of information to manageable size while still retaining statistical validity. For some purposes, however, it might be of value to know the various sources of variance which may affect the concentration of an individual element, and such information cannot be obtained

Table 4. Composition of colloidal material in suspension, expressed as oxides

Experiment Number*	Experiment Identification Code*	K ₂ O mg/L	CaO mg/L	MgO mg/L	Al ₂ O ₃ mg/L	SiO ₂ mg/L	Composition					Fe ₂ O ₃ mg/L	Total Colloids mg/L
1	S t20FW	37.0	4.25	22.90	286	466	K _{0.10}	Ca _{0.01}	Mg _{0.07}	Al _{0.72}	SiO _{3.20}	27.2	843
3	S t44FW	20.8	2.12	7.39	115	211	K _{0.12}	Ca _{0.01}	Mg _{0.05}	Al _{0.64}	SiO _{3.08}	28.3	384
5	S t92FW	12.3	3.06	7.69	127	242	K _{0.06}	Ca _{0.01}	Mg _{0.05}	Al _{0.62}	SiO _{3.02}	29.1	421
7	S T20FW	28.2	0.59	1.08	380	574	K _{0.06}	Ca _{0.001}	Mg _{0.003}	Al _{0.78}	SiO _{3.20}	73.6	1057
9	S T44FW	-	-	-	176	289				Al _{0.36}	SiO _{2.54}	32.8	497
11	S T92FW	16.6	2.83	7.20	148	332	K _{0.07}	Ca _{0.01}	Mg _{0.03}	Al _{0.52}	SiO _{2.86}	26.7	533
25	SB t20FW	2.4	0.84	2.14	257	445	K _{0.008}	Ca _{0.002}	Mg _{0.007}	Al _{0.68}	SiO _{3.03}	57.3	765
27	SB t44FW	51.2	0.29	1.10	34.7	25	K _{2.57}	Ca _{0.01}	Mg _{0.07}	Al _{1.62}	SiO _{5.80}	6.3	119
29	SB t92FW	4.1	1.78	2.19	54.9	62	K _{0.08}	Ca _{0.03}	Mg _{0.05}	Al _{1.05}	SiO _{3.70}	11.6	137
31	SB T20FW	7.6	0.00	0.08	83.1	147	K _{0.07}		Mg _{0.001}	Al _{0.67}	SiO _{3.04}	16.3	254
33	SB T44FW	9.0	0.39	-	3.8	27	K _{0.44}	Ca _{0.02}		Al _{0.18}	SiO _{2.51}	1.0	41
35	SB T92FW	0.0	1.15	-	4.7	79		Ca _{0.02}		Al _{0.08}	SiO _{2.14}	1.1	86

* See Fig. 1 for experimental conditions and explanation of experiment identification code

- = not determined

easily from the above paper. To provide this information an ANOVA was run on the analytical data from the aqueous phase from which colloid had been removed for experiments 1 to 48, and the results are summarized in the Appendix. The elements are listed in the order they appear in Boon and Hitchon, 1983a, Table 5.

EXPERIMENTS 49 TO 72 ("BLANK" RUNS)

Of the 24 experiments which effectively represent "blank" runs to test contamination effects of the autoclaves, only those of 92 hours duration were carried out, that is, experiments number 53, 54, 59, 60, 65, 66, 71 and 72. Because the autoclaves used in the experiments reported by Boon and Hitchon (1983a, b) were composed of several different materials some of these "blank" runs were repeated with different autoclaves. The composition of the aqueous fluids obtained from the 16 runs made to test contamination effects are given in Table 5, together with information on the autoclave material used for each run. Concentrations of effectively all elements except Cr were generally very low compared to the corresponding amount in the experiments with shale present, and the Cr concentrations far exceeded those in the experiments with shale or with bitumen alone, and were much higher in the high pH solutions. With the exception of Cr, it can be stated that the 16 experiments reported here indicate that contamination from the autoclaves is effectively negligible.

EXPERIMENTS 73 TO 96

These experiments represent runs to test the effects of pH, temperature, time and salinity on the removal of trace elements from bitumen. The chemical composition of the aqueous phase from these experiments is shown in Table 6. The most dramatic effect is the reduction in pH to the range 2.5 to 3.2 for those experiments in which pH was not controlled by the addition of borax. As expected, this resulted in significantly increased contents of Fe, Mn, and Zn at higher temperatures, due to

Table 5. Chemical composition of the aqueous phase obtained from the "blank" runs

Experiment Number**	Experiment Identification Code*	Autoclave Material**	Li mg/L	Na mg/L	K mg/L	Mg mg/L	Ca mg/L	Sr mg/L	Al mg/L	As µg/L	Cr µg/L	Cu µg/L	Fe mg/L	Hg µg/L	Mn mg/L	Ti mg/L	V µg/L	Zn mg/L	SiO ₂ mg/L	PO ₄ (total) mg/L	H ₃ BO ₃ mg/L
53	t92FW	Ti	ND	ND	ND	0.1	Tr	Tr	ND	ND	1080	Tr	ND	0.1	Tr	Tr	ND	ND	1.2	ND	0.3
54	t92SW	Ti	ND	2100	Tr	Tr	Tr	Tr	ND	ND	50	Tr	Tr	0.1	ND	Tr	Tr	0.02	1.2	2.5	0.4
59	T92FW	TiPd	ND	8	ND	0.1	1	Tr	ND	ND	5040	20	Tr	Tr	Tr	Tr	20	0.05	10.4	4.9	0.6
59	T92FW	Inc	ND	ND	ND	0.1	1	Tr	ND	ND	1800	Tr	ND	Tr	ND	ND	Tr	0.03	0.8	ND	0.6
59	T92FW	316SS	ND	2	ND	0.1	Tr	Tr	ND	ND	700	Tr	ND	Tr	0.1	Tr	ND	ND	3.3	ND	0.4
60	T92SW	TiPd	ND	2130	Tr	Tr	Tr	Tr	ND	ND	ND	Tr	ND	0.2	ND	ND	ND	ND	0.6	3.7	0.3
60	T92SW	Inc	ND	2260	1	0.1	Tr	Tr	ND	ND	100	20	ND	0.1	Tr	ND	ND	0.07	0.5	ND	0.1
60	T92SW	316SS	ND	2000	1	0.1	2	Tr	ND	ND	ND	290	0.1	Tr	0.5	Tr	20	0.03	8.7	2.2	1.5
65	bt92FW	Ti	ND	470	ND	Tr	ND	Tr	ND	ND	2940	ND	0.1	0.2	ND	Tr	Tr	0.03	0.6	ND	-
66	bt92SW	Ti	ND	2710	4	Tr	Tr	Tr	ND	ND	26300	ND	0.1	Tr	ND	Tr	20	0.03	2.2	ND	-
71	bt92FW	TiPd	ND	510	1	Tr	Tr	Tr	1.8	ND	83700	Tr	0.1	Tr	ND	Tr	60	0.20	1.5	ND	-
71	bt92FW	Inc	ND	500	ND	Tr	ND	ND	0.2	ND	18700	ND	0.1	0.1	ND	Tr	10	0.03	0.9	ND	-
71	bt92FW	316SS	ND	510	ND	Tr	ND	Tr	0.6	5	15200	ND	Tr	Tr	ND	Tr	30	0.02	4.7	ND	-
72	bt92SW	TiPd	ND	2820	1	Tr	ND	Tr	0.1	ND	6500	ND	Tr	Tr	ND	Tr	Tr	0.02	1.4	ND	-
72	bt92SW	Inc	ND	2660	4	ND	ND	Tr	0.3	ND	78500	Tr	Tr	0.1	ND	Tr	40	0.20	1.4	1.8	-
72	bt92SW	316SS	ND	2640	5	ND	Tr	Tr	0.6	10	114000	Tr	Tr	ND	ND	Tr	230	0.23	5.4	ND	-

* See Fig. 1 for experimental conditions and explanation of experiment identification code

** Ti = Titanium
 TiPd = Titanium + 0.2% Pd
 Inc = Inconel
 316SS = 316 stainless steel

ND = Not detected
 Tr = trace (<0.05 mg/L; except K and Ca < 1mg/L, Cu and V < 10 µg/L, Hg < 0.1 µg/L)

Table 6. Chemical composition of the aqueous phase obtained from experiments 73 to 96 following filtration through 0.45 μm Millipore filters

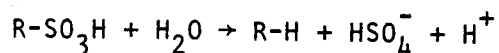
Experiment Number *	Experiment Identification Code*	Li mg/L	Na mg/L	K mg/L	Mg mg/L	Ca mg/L	Sr mg/L	Al mg/L	As $\mu\text{g/L}$	Cr $\mu\text{g/L}$	Cu $\mu\text{g/L}$	Fe mg/L	Hg $\mu\text{g/L}$	Mn mg/L	Pb mg/L	Ti mg/L	V $\mu\text{g/L}$	Zn mg/L	NH ₃ mg/L	SiO ₂ mg/L	F mg/L	Cl mg/L	HCO ₃ mg/L	SO ₄ mg/L	PO ₄ (total) mg/L	PO ₄ (ortho) mg/L	H ₃ BO ₃ mg/L	pH	Total Organic Carbon mg/L
73	B t20FW	ND	1	Tr	ND	Tr	Tr	0.3	25	10	80	2.7	0.2	0.1	ND	ND	ND	0.05	0.7	1.0	ND	98	ND	15.6	ND	0.6	0.6	2.5	57
74	B t20SW	Tr	2140	Tr	ND	Tr	Tr	0.2	25	30	240	2.0	0.5	2.8	0.1	Tr	30	Tr	0.5	2.8	ND	3540	1	7.1	3.1	0.1	0.4	2.9	45
75	B t44FW	Tr	7	Tr	ND	Tr	Tr	0.4	15	10	30	1.2	0.3	0.2	ND	Tr	Tr	Tr	0.4	1.0	ND	58	ND	11.7	ND	0.4	0.3	3.1	44
76	B t44SW	Tr	2110	Tr	ND	Tr	Tr	0.2	25	20	50	2.6	0.3	0.5	0.1	Tr	Tr	Tr	0.4	0.9	ND	3500	ND	13.5	2.1	0.6	0.3	2.9	60
77	B t92FW	ND	1	Tr	ND	Tr	ND	0.2	40	20	10	4.8	0.2	0.2	ND	Tr	20	Tr	0.3	1.0	ND	72	ND	16.1	ND	0.4	0.4	2.9	42
78	B t92SW	Tr	2390	Tr	ND	1	Tr	0.1	ND	30	20	10.1	0.2	0.7	ND	ND	Tr	Tr	0.3	1.7	ND	3580	ND	14.8	2.2	0.2	0.3	2.9	42
79	B T20FW	ND	3	1	Tr	Tr	Tr	ND	20	10	20	7.6	0.2	0.3	ND	ND	ND	0.09	0.6	4.6	0.1	90	ND	18.0	ND	0.9	0.7	2.8	52
80	B T20SW	Tr	2330	Tr	ND	Tr	Tr	ND	25	60	Tr	27.0	0.2	0.6	ND	Tr	Tr	0.13	0.6	2.4	0.1	3680	ND	19.2	1.5	0.3	1.3	2.7	51
81	B T44FW	ND	22	1	0.1	1	Tr	0.3	25	50	40	23.9	0.5	0.8	ND	Tr	30	0.49	0.6	3.7	0.1	88	ND	15.0	ND	0.7	2.5	3.2	67
82	B T44SW	Tr	2070	1	Tr	Tr	Tr	0.2	25	50	20	21.0	0.1	0.5	ND	Tr	10	0.26	0.5	3.0	ND	3640	ND	17.3	ND	0.5	1.2	3.1	53
83	B T92FW	ND	2	1	ND	Tr	Tr	0.2	20	10	ND	163.0	0.2	0.5	0.1	ND	Tr	0.21	0.4	2.6	ND	74	ND	15.9	ND	0.3	1.2	3.1	64
84	B T92SW	Tr	2620	Tr	ND	Tr	Tr	ND	40	30	10	18.8	0.2	0.4	ND	Tr	20	0.17	0.3	2.6	ND	3600	ND	16.1	ND	0.4	1.1	3.1	53
85	Bbt20FW	Tr	499	Tr	ND	Tr	Tr	0.3	15	1560	20	0.5	0.3	Tr	0.2	Tr	60	Tr	0.2	1.4	ND	128	11	11.4	ND	0.2	-	8.8	189
86	Bbt20SW	Tr	3020	Tr	ND	Tr	Tr	0.6	25	270	20	0.5	0.3	Tr	0.2	Tr	20	Tr	0.2	2.8	ND	3510	3	4.5	1.5	0.4	-	8.7	62
87	Bbt44FW	Tr	513	Tr	0.1	Tr	Tr	0.3	25	1230	Tr	0.5	0.3	ND	ND	Tr	20	ND	0.2	3.2	ND	128	14	15.3	ND	0.1	-	8.9	86
88	Bbt44SW	0.06	2810	Tr	0.1	Tr	Tr	0.3	ND	2780	30	0.5	0.6	ND	ND	Tr	20	ND	0.3	1.3	ND	3530	12	11.4	ND	0.1	-	8.8	138
89	Bbt92FW	Tr	494	Tr	ND	Tr	Tr	0.5	25	70	ND	0.5	0.5	Tr	ND	Tr	20	Tr	0.3	4.8	ND	72	13	17.1	ND	0.1	-	8.8	167
90	Bbt92SW	0.06	2840	Tr	ND	Tr	Tr	0.4	25	120	Tr	0.6	0.5	Tr	ND	Tr	20	Tr	0.3	3.3	ND	2690	18	18.9	2.2	0.1	-	8.8	162
91	Bbt20FW	Tr	534	Tr	ND	Tr	Tr	0.5	20	100	80	0.6	0.5	0.1	0.4	Tr	80	0.12	0.3	3.7	ND	64	18	20.3	4.0	0.5	-	8.8	212
92	Bbt20SW	0.05	2980	Tr	ND	Tr	Tr	0.6	20	90	20	0.5	0.6	Tr	ND	Tr	50	Tr	0.4	2.7	ND	3530	18	22.5	1.5	0.1	-	8.7	242
93	Bbt44FW	Tr	530	Tr	0.1	Tr	Tr	0.2	35	10	Tr	0.5	0.3	ND	ND	Tr	60	ND	0.3	2.5	ND	81	20	26.6	ND	0.1	-	8.9	225
94	Bbt44SW	Tr	2540	Tr	0.1	Tr	Tr	0.2	15	10	Tr	0.5	0.5	ND	ND	Tr	30	ND	0.3	4.1	ND	3530	20	29.1	3.1	1.7	-	8.7	195
95	Bbt92FW	Tr	497	Tr	ND	Tr	Tr	0.2	45	40	ND	0.5	0.6	Tr	ND	ND	30	ND	0.3	2.5	ND	66	10	26.4	ND	0.1	-	8.9	225
96	Bbt92SW	0.06	2400	Tr	ND	Tr	Tr	0.1	20	60	ND	0.6	0.6	Tr	ND	Tr	40	Tr	0.3	2.0	ND	2720	22	30.0	ND	2.0	-	8.8	188

* See Fig. 1 for experimental conditions and explanation of experiment identification code

ND = Not detected

Tr = trace (<0.05 mg/L; except K and Ca <1 mg/L, Cu and V <10 $\mu\text{g/L}$)

dissolution of these metals from the stainless steel frame of the weighing boats. As noted by Boon and Hitchon (1983a) for the experiments with shale, total organic carbon is much higher at high pH levels than at low pH levels, probably due to increased ionization of functional groups in the bitumen with consequent increased solubility in the aqueous phase of the organic compounds containing these groups. Sulphate is higher in the high pH solutions reacted with bitumen at 250°C for 44 hours or longer, possible due to a hydrolytic desulphurization reaction of the sulphonic acid group of the bitumen:



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APPENDIX

ANOVA for individual element concentrations
Experiments 1 to 48

LEGEND

B = Bitumen effect
b = pH effect
T = Temperature effect
H = Time effect
S = Salinity effect

Li

b: decreases Li
T: increases Li
H: increases Li
S: increases Li dramatically ($\alpha \leq 10^{-7}$)
TS: temperature has little effect in fresh water, more in saline water, but the effect of salinity is enhanced about 2½ times by temperature
HS: time has little effect in fresh water, but in saline water Li increases with time

K

B: slightly increases K (17 to 21 mg/L)
b: decreases K (30 to 8 mg/L)
T: slightly increases K (17 to 20 mg/L)
S: increases K (8 to 31 mg/L)
bT: without pH control, temperature increases K (24 to 36 mg/L)
with pH control, temperature decreases K (10 to 6 mg/L)
i.e. pH control decreases K much more at 250°C than at 200°C
(36 to 6 vs 24 to 10)
bS: salinity has a much smaller effect when pH is controlled
bTS: without pH control - effect of S, factor 4 at both temperatures
- effect of T, factor 1.5 at both salinities
with pH control - effect of S, factor 4 at 200°C and factor 10
at 250°C

- effect of T, factor $\frac{1}{4}$ in freshwater and $\frac{5}{8}$ in saltwater

Mg

- B: increases Mg (0.5 to 0.7 mg/L)
- b: decreases Mg (0.9 to 0.3 mg/L)
- S: increases Mg (0.3 to 0.9 mg/L)
- Bb: bitumen increases Mg without pH control, but has hardly any effect when pH is controlled
- bS: salinity has much less effect when the pH is controlled than when it is not controlled
- TS: temperature increases Mg very slightly in freshwater but decreases it in saline waters, i.e. the effect of salinity is much less at higher temperatures
- HS: Mg increases with time in fresh water but decreases with time in saline solutions, even though the Mg content of the latter is always higher than in the former
- bTS: without pH control - temperature decreases Mg in saline solutions and increases it in fresh water
- salinity increases Mg at both temperatures
with pH control - temperature does not affect Mg in saline solutions, but decreases it in fresh water
- bHS: without pH control - time decreases Mg in saline solutions and increases it in fresh water
with pH control - time increases Mg very slightly in both saline solutions and freshwater, but the effect of salinity is generally small at all times.

Ca

- B: increases Ca (6 to 8 mg/L)
- b: decreases Ca (11 to 3 mg/L)

- S: increases Ca (1 to 13 mg/L)
- BS: bitumen has no effect in fresh water, but increases Ca in the saline solutions (10 to 15 mg/L)
- bS: pH control results in a decrease of the effect of salinity by about four times

Sr

- b: decreases Sr (0.5 to 0.1 mg/L)
- S: increases Sr (0.1 to 0.5 mg/L)
- bS: the effect of salinity is very much smaller when the pH is controlled

Al

- b,S, bS: when pH is controlled, Al increase more in freshwater than saline solutions

As

No significant effects

Cr

- B: decreases Cr (50 to 15 $\mu\text{g/L}$)
 - b: decreases Cr (60 to 10 $\mu\text{g/L}$)
 - S: decreases Cr (50 to 15 $\mu\text{g/L}$)
 - BS: the decrease of Cr caused by salinity is much smaller in the presence of bitumen i.e. bitumen has little effect in saline solutions
 - bS: when pH is controlled, salinity is less effective in decreasing Cr
 - BbS: without bitumen - both pH control and salinity cause a very substantial decrease in Cr, but once one of these has been added, the addition of the other results in only a minimal effect
- with bitumen - salinity has only a small effect, whether or not

the pH is controlled; Cr contents are much lower, in general, than when bitumen is absent

Cu

No significant effects

Fe

No significant effects

Hg

S: decreases Hg (1.5 to 0.7 µg/L)

Mn

b: sharply decreases Mn (1.0 to 0.1 mg/L)

S: sharply increases Mn (0.2 to 0.9 mg/L)

BS: salinity has a stronger effect in the presence of bitumen; in freshwater bitumen decreases Mn, and in saline solutions increases Mn

bS: the effect of salinity is small (in absolute terms) when pH is controlled, and both the freshwater and saline solutions exhibit a decrease in Mn when pH is controlled

BbS: without bitumen - salinity increases Mn if pH is not controlled but there is no effect with pH control
- control of pH results in decreased Mn, to about the same level, in both freshwater and saline solutions

with bitumen - salinity increases Mn whether or not pH is controlled

- pH control decreases Mn in both freshwater and saline solutions, but by a smaller factor than when bitumen is absent. In fresh water, bitumen decreases Mn if pH is not controlled, otherwise there is no effect. In saline solutions the

presence of bitumen increases Mn whether or not
pH is controlled

Ti

- B: decreases Ti (0.3 to 0.2 mg/L)
- S: decreases Ti (0.5 mg/L to Trace)
- BS: in saline solutions Ti is very low, although when bitumen is present there is slightly less Ti; in fresh water the presence of bitumen causes a significant decrease in Ti i.e. both salinity and bitumen exert the same effect, but salinity is more effective than the presence of bitumen in reducing the Ti content

V

- S: decreases V (90 to 30 µg/L)

Zn

- b: decreases Zn (0.14 to 0.03 mg/L)
- T: decreases Zn (0.10 to 0.07 mg/L)
- S: increases Zn (0.04 to 0.12 mg/L)
- BS: in fresh water the presence of bitumen decreases Zn slightly, whereas in saline solutions it increases Zn slightly
- bS: salinity has no effect when pH is controlled
- BbS: without bitumen - salinity has no effect when pH is controlled
with bitumen - salinity has only a very small effect when pH is controlled; bitumen decreases Zn in fresh water and increases it in saline solutions

NH₃

- S: doubles NH₃ contents

SiO₂

- T: increases SiO₂
- H: increases SiO₂

F

- T: increases F (2.2 to 2.6 mg/L)
- H: increases F (2.1 to 2.4 to 2.6 mg/L)
- S: decreases F (2.6 to 2.1 mg/L)
- bT: when pH is controlled, F is decreased at 200°C and increased at 250°C; temperature slightly decreases F when pH is not controlled, but increases it sharply when pH is controlled
- bS: salinity has more effect when pH is not controlled than when it is controlled
- HS: time has a consistent effect only in fresh water

SO₄

No significant effects

PO₄ (total)

- S: decreases PO₄ (total) (6.5 to 2.6 mg/L)

PO₄ (ortho)

- b: decreases PO₄ (ortho)
- S: decreases PO₄ (ortho)

Total Organic Carbon

- b: significantly increases Total Organic Carbon (73 to 174 mg/L)

pH

- b: increases pH (6.9 to 7.5)
- T: decreases pH (7.4 to 7.0)
- S: decreases pH (7.6 to 6.8)
- TS: salinity has a stronger effect at 250°C than at 200°C, but is very noticeable in both cases, whereas the effect of temperature only becomes significant in the saline solutions.