Appendix 1
Water composition

Contents

A1.1 Analyses

All water analyses reported in this appendix were performed at the Laboratory of Analyses and Applied Radiochemistry, Nuclear Chemistry and Services (SCK•CEN, Belgium). The analyses techniques are briefly described by De Craen *et al.* (in preparation).

A1.1.1 Total organic carbon (TOC) and total inorganic carbon (TIC) content

The total organic carbon content (TOC) is measured with a high-temperature TOC analyser. The total carbon content (TC) is determined by injection of an aliquot of the sample, without any pre-treatment, in a combustion tube at 680°C. Catalytic oxidation transforms the sample completely to CO_2 and H_2O. After drying, the CO_2 concentration is measured by an infrared detector. The total inorganic carbon content (TIC) is determined by injection of an aliquot of the sample, without any pre-treatment, in a reactor which contains acidified water (20% H_3PO_4) at room temperature. In this acidic environment, all forms of TIC are purged out of the solution as CO_2. After drying, the CO_2 concentration is measured by an infrared detector. The total organic carbon content (TOC) is made by the difference of TC and TIC. TOC measurements were performed with a Dohrman DC-190 High Temperature TOC analyser.

A1.1.2 Cation concentration

The cation concentration (Na, K, Mg, Ca, Fe, Si) and that of boron (B) in water are measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). Samples are usually diluted ten times and acidified to 1% HNO_3 / 5% HCl (higher dilutions may be necessary when the concentrations are too high). The diluted samples are filtered through a 0.45 μm filter before analysis.

A1.1.3 Anion concentration

Ion chromatography (IC) is used for the analyses of the anions Cl^-, Br^-, SO_4^{2-} and HPO_4^{2-}. To avoid overload of the separation column, samples are usually diluted ten times. The diluted samples are analysed by the use of a classical ion chromatograph with a 1.8 mM Na_2CO_3 / 1.7 mM $NaHCO_3$ solution as eluent.
Ion selective electrode (ISE) is used for measuring the F^- concentration. Samples (and standards) are diluted with TISAB (Total Ionic Strength Adjustment Buffer), which provides a nearly uniform ionic strength background, adjusts *p*H and breaks up complexes. The fluoride concentration is determined by direct potentiometry using a combined fluoride / reference electrode.

A1.1.4 Uranium concentration

The uranium (U) concentration is measured by Inductively Coupled Plasma-Mass Spectrometry (Elan 5000, Perkin Elmer ICP-MS). The samples are first diluted in 2 % nitric acid short before analysis. An internal standard is added to improve the precision and to correct for matrix effects.

A1.1.5 Ionic strength

The ionic strength, I, is defined as:

$$I = \frac{1}{2} \Sigma(C_i \cdot Z_i^2)$$

where C is the concentration ($mol \cdot l^{-1}$) and Z the charge (*e.g.* 2 for Ca^{2+}) of ion *i*. The summation is carried out for all ions in solution. The ionic strength given in the tables below was calculated by considering the following charged species: Na^+, K^+, Mg^{2+}, Ca^{2+}, HCO_3^-, Cl^-, F^-, Br^-, SO_4^{2-} and HPO_4^{2-}. Boron (B), silicon (Si) and iron (Fe) were not taken into account since they are expected to occur as neutral species: $B(OH)_3(aq)$, $SiO_2(aq)$ and $FeCO_3(aq)$ as indicated in Table 1.8 of Chapter 1.

A1.1.6 Charge imbalance

The accuracy of a water analysis is normally assessed by the degree of charge imbalance calculated from the given water composition. The principle of electroneutrality requires that the ionic species in any water sample must remain charge balanced. The degree of charge imbalance is thus a measure for the error of a water analysis:

$$\text{Charge Imbalance (\%)} = \frac{(sum\ cations - sum\ anions)}{(sum\ cations + sum\ anions)} \times 100$$

where cations and anions are expressed in $eq \cdot l^{-1}$ or $meq \cdot l^{-1}$. An acceptable charge imbalance should be less than 5% for a good water analysis (Appelo and Postma, 1999).
The same charged species than those taken into account for the determination of I are considered. Major contributions of cationic charge are from Na^+, K^+, Ca^{2+}, and Mg^{2+}. Negative charges are from the total alkalinity and anions Cl^-, F^-, Br^-, and SO_4^{2-}. In most natural waters, acid-base systems other than aqueous carbonate can often be neglected and the total alkalinity in $eq \cdot l^{-1}$ or $meq \cdot l^{-1}$ is conventionally defined by (Stumm and Morgan, 1996; Langmuir, 1997):

$$\text{Total alkalinity} = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] - [H^+]$$

where [ ] refers to molarity of different species.
In our calculations, the HCO_3^- concentration was used to approximate the total alkalinity. The bicarbonate concentration is derived from the total inorganic carbon (TIC) concentration:

$$HCO_3^- \ (mg \cdot l^{-1}) = TIC\,(mgC \cdot l^{-1}) \times \frac{M_{HCO_3^-}}{M_C}$$

where M is the molecular and atomic weight of HCO_3^- and C, respectively.
The charge balance equation for Boom Clay pore water can therefore be simplified to:

$$[Na^+] + [K^+] + 2\,[Ca^{2+}] + 2\,[Mg^{2+}] = [HCO_3^-] + [Cl^-] + [F^-] + [Br^-] + 2\,[SO_4^{2-}]$$

where [ ] refers to molarity of different species.

The high values of charge imbalance are specifically found for BCW (see A1.3). The high *p*H value (around 9.5) at the time of analyses indicates that BCW experiences CO_2 degassing. For SBCW, the *p*H is much less sensible to CO_2

degassing since it is mainly controlled by the bicarbonate concentration that is fixed by the dissolution of the $NaHCO_3$ salt. The use of HCO_3^- concentration to represent the total alkalinity at *p*H around 9 underestimated the total negative charges of the water by neglecting the contribution of OH^- and CO_3^{2-}. The approximation that the equivalent of HCO_3^- is equal to the total alkalinity is only valid at *p*H below about 8.3 (Langmuir, 1997). A precise charge imbalance at higher *p*H should be calculated using the total alkalinity. Indeed, the total alkalinity is a conservative value since it accounts for HCO_3^-, CO_3^{2-} and *p*H changes.

A1.2 Synthetic Boom Clay water

A1.2.1 Complexation tests

	Cp-2 **mol·l^{-1}**	**Cp-3** **mol·l^{-1}**	**Cp-5/6** **mol·l^{-1}**	**Cp-7** **mol·l^{-1}**
Na^+	1.45×10^{-2}	1.40×10^{-2}	1.58×10^{-2}	1.67×10^{-2}
K^+	3.48×10^{-4}	3.48×10^{-4}	4.12×10^{-4}	3.63×10^{-4}
Mg^{2+}	1.10×10^{-4}	1.05×10^{-4}	1.70×10^{-4}	1.74×10^{-4}
Ca^{2+}	9.11×10^{-5}	6.51×10^{-5}	1.22×10^{-4}	7.59×10^{-5}
$HCO_3^{-\#}$	1.31×10^{-2}	1.33×10^{-2}	1.42×10^{-2}	1.38×10^{-2}
Cl^-	7.87×10^{-4}	7.76×10^{-4}	9.31×10^{-4}	8.43×10^{-4}
F^-	2.61×10^{-4}	2.72×10^{-4}	2.95×10^{-4}	2.74×10^{-4}
SO_4^{2-}	3.85×10^{-6}	3.75×10^{-6}	5.10×10^{-6}	3.85×10^{-6}
HPO_4^{2-}	7.74×10^{-5}	$<5.21\times10^{-6}$	1.49×10^{-5}	$<5.21\times10^{-6}$
B	7.83×10^{-4}	7.90×10^{-4}	9.34×10^{-4}	8.97×10^{-4}
TOC (mg·l^{-1})	<10	<10	<11	<11
TIC (mg·l^{-1})	127	160	171	166
Ionic strength	1.51×10^{-2}	1.47×10^{-2}	1.65×10^{-2}	1.65×10^{-2}
Charge imbalance (%)	3.4	0.9	4.0	8.1

derived from the TIC by considering that all inorganic carbon occurs as HCO_3^- at *p*H ~ 8.2.

A1.2.2 Solubility tests

	S-5/7/8 **mol·l^{-1}**	**S-9/10** **mol·l^{-1}**	**S-12/13** **mol·l^{-1}**
Na^+	1.39×10^{-2}	1.44×10^{-2}	1.44×10^{-2}
K^+	3.86×10^{-4}	3.71×10^{-4}	3.58×10^{-4}
Mg^{2+}	1.23×10^{-4}	1.23×10^{-4}	1.11×10^{-4}
Ca^{2+}	5.69×10^{-5}	7.29×10^{-5}	6.19×10^{-5}
$HCO_3^{-\#}$	1.39×10^{-2}	1.32×10^{-2}	1.41×10^{-2}
Cl^-	8.21×10^{-4}	7.93×10^{-4}	7.93×10^{-4}
F^-	2.74×10^{-4}	2.68×10^{-4}	2.79×10^{-4}
SO_4^{2-}	2.81×10^{-6}	4.06×10^{-6}	3.64×10^{-6}
HPO_4^{2-}	—	—	$<5.21\times10^{-6}$
B	6.57×10^{-4}	9.43×10^{-4}	7.40×10^{-4}
Fe	2.35×10^{-5}	3.58×10^{-6}	2.69×10^{-6}
TOC (mg·l^{-1})	<12	<11	<12
TIC (mg·l^{-1})	167	158	169
Ionic strength	1.50×10^{-2}	1.49×10^{-2}	1.53×10^{-2}
Charge imbalance (%)	-1.1	3.0	-0.3

derived from the TIC by considering that all inorganic carbon occurs as HCO_3^- at *p*H ~ 8.2.

A1.2.3 Sorption test

	Sp-1 **mol·l^{-1}**
Na^+	1.48×10^{-2}
K^+	3.38×10^{-4}
Mg^{2+}	1.09×10^{-4}
Ca^{2+}	6.39×10^{-5}
$HCO_3^{-\#}$	1.36×10^{-2}
Cl^-	9.03×10^{-4}
F^-	2.84×10^{-4}
SO_4^{2-}	3.12×10^{-6}
HPO_4^{2-}	—
B	8.14×10^{-4}
Fe	$<8.95\times10^{-7}$
TOC (mg·l^{-1})	<11
TIC (mg·l^{-1})	163
Ionic strength	1.53×10^{-2}
Charge imbalance (%)	2.3

derived from the TIC by considering that all inorganic carbon occurs as HCO_3^- at *p*H ~ 8.2.

A1.3 Boom Clay water

A1.3.1 Solubility tests

	S-2 **mol·l^{-1}**	**S-2'/3** **mol·l^{-1}**	**S-6** **mol·l^{-1}**	**S-11** **mol·l^{-1}**
Na^+	1.74×10^{-2}	1.78×10^{-2}	1.83×10^{-2}	1.78×10^{-2}
K^+	2.20×10^{-4}	2.40×10^{-4}	3.09×10^{-4}	2.51×10^{-4}
Mg^{2+}	1.08×10^{-4}	1.23×10^{-4}	1.16×10^{-4}	1.28×10^{-4}
Ca^{2+}	7.73×10^{-5}	8.48×10^{-5}	9.23×10^{-5}	9.48×10^{-5}
$HCO_3^{-\#}$	1.43×10^{-2}	1.53×10^{-2}	1.44×10^{-2}	1.73×10^{-2}
Cl^-	7.16×10^{-4}	7.19×10^{-4}	7.45×10^{-4}	7.76×10^{-4}
F^-	1.49×10^{-4}	1.61×10^{-4}	1.64×10^{-4}	1.67×10^{-4}
SO_4^{2-}	$<2.60\times10^{-6}$	$<2.60\times10^{-6}$	4.79×10^{-6}	$<2.60\times10^{-6}$
HPO_4^{2-}	2.53×10^{-5}	—	—	2.89×10^{-5}
Br^-	6.88×10^{-6}	9.76×10^{-6}	6.26×10^{-6}	6.26×10^{-6}
Si	7.83×10^{-5}	8.90×10^{-5}	7.83×10^{-5}	7.83×10^{-5}
B	7.31×10^{-4}	7.40×10^{-4}	7.58×10^{-4}	7.03×10^{-4}
Fe	1.36×10^{-5}	1.65×10^{-5}	2.47×10^{-5}	3.03×10^{-5}
U	$<2.10\times10^{-9}$	$<2.10\times10^{-9}$	6.30×10^{-9}	6.30×10^{-9}
TOC (mg·l^{-1})	110	110	110	120
TIC (mg·l^{-1})	172	184	173	208
*p*H*	9.2	—	9.6	8.2
Ionic strength	1.68×10^{-2}	1.76×10^{-2}	1.74×10^{-2}	1.87×10^{-2}
Charge imbalance (%)	8.2	6.6	10.7	0.5

derived from the TIC by considering that all inorganic carbon occurs as HCO_3^-
* at time of analyses

A1.3.2 Sorption tests

	Sp-2 **mol·l^{-1}**	**Sp-4** **mol·l^{-1}**
Na^+	1.83×10^{-2}	1.78×10^{-2}
K^+	3.09×10^{-4}	2.51×10^{-4}
Mg^{2+}	1.16×10^{-4}	1.28×10^{-4}
Ca^{2+}	9.23×10^{-5}	9.48×10^{-5}
$HCO_3^{-\#}$	1.44×10^{-2}	1.73×10^{-2}
Cl^-	7.45×10^{-4}	7.76×10^{-4}
F^-	1.64×10^{-4}	1.67×10^{-4}
SO_4^{2-}	4.79×10^{-6}	$<2.60\times10^{-6}$
HPO_4^{2-}	—	2.89×10^{-5}
Br^-	6.26×10^{-6}	6.26×10^{-6}
Si	7.83×10^{-5}	7.83×10^{-5}
B	7.58×10^{-4}	7.03×10^{-4}
Fe	2.47×10^{-5}	3.03×10^{-5}
U	6.30×10^{-9}	6.30×10^{-9}
TOC (mg·l^{-1})	130	130
TIC (mg·l^{-1})	173	208
*p*H*	9.6	8.2
Ionic strength	1.74×10^{-2}	1.87×10^{-2}
Charge imbalance (%)	10.7	0.5

derived from the TIC by considering that all inorganic carbon occurs as HCO_3^-

* at time of analyses

A1.4 References

Appelo, C. A. J., Postma, D. (1999) "Geochemistry, groundwater and pollution". A. A. Balkema, Rotterdam.

De Craen, M., Wang, L., Van Geet, M., Moors, H. 2004. Geochemistry of the Boom Clay pore water a the Mol site. SCK•CEN report, **BLG-xxx**, Mol, Belgium. *In preparation.*

Langmuir, D. 1997. "Aqueous environmental geochemistry". Prentice Hall, New Jersey.

Stumm, W., Morgan, J.J. 1996. "Aquatic Chemistry, 3rd ed.", John Wiley & Sons, New York.