

1997/AB/046



97/C072023/AD/mvo/P-20



STUDIECENTRUM VOOR KERNENERGIE
CENTRE D'ÉTUDE DE L'ÉNERGIE NUCLÉAIRE

Boom Clay *in situ* porewater chemistry

Ann Dierckx

BLG-734

Waste and Disposal Unit
SCK•CEN, Belgian Nuclear Research Centre,
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1. Introduction

The Boom Clay Formation is studied as a candidate host rock for the disposal of radioactive waste in Belgium. The layer is located between 180 and 280 m deep at the Mol site. Originally, the intention of writing this report was to define one unique Boom Clay *in situ* porewater chemistry. Unfortunately, the frequency of sampling different piezometers in the clay layer is rather low. In this report, we will give a mean value (of 11 measurements) for the ionic composition of the Experimental Gallery Bottom Shaft (EG/BS) piezometer, and compare single analyses of other piezometers with this value.

The EG/BS piezometer was one of the first piezometers installed. It is installed at a depth of -260 m and in contact with the Silty Layer of the Boom Clay Formation. After the installation of the piezometer, the borehole was filled with uncharacterised material (gravel). This may be a reason for the difference of pH (~9.5) and $p\text{CO}_2$ $10^{-3.72}$ atm (Dierckx in Aertsens *et al.*, 1995) of EG/BS clay water compared to other measurements and calculations. The pH and $p\text{CO}_2$ will be discussed in separate paragraphs, as will be the Total Organic Carbon (TOC) content and the redox potential.

2. $p\text{CO}_2$

The CO_2 partial pressure has been measured by Henrion *et al.* (1985). A value of $10^{-2.5}$ atm has been reported.

Calculations by Dierckx in Aertsens *et al.* (1995), based on data resulting from the Archimède project (Griffault *et al.*, 1996) give a $p\text{CO}_2$ value of $10^{-2.42}$ atm. The CO_2 partial pressure of the groundwater is thus oversaturated with respect to atmospheric conditions ($p\text{CO}_2 = 10^{-3.5}$ atm).

3. pH

Because of the oversaturation of CO_2 in the clay water, special precautions must be taken during the measurement of the pH to avoid a degassing of the clay water, especially if one lowers the pressure from over 1 MPa to 0.1 MPa. The value reported here is the value measured *in situ* with an optode (Griffault *et al.*, 1996) and equals 8.20 +/- 0.05.

4. Redox potential

The best estimate value for the redox potential equals -250 mV (SHE).

5. Total organic carbon content

The Boom Clay is a 35 million years old marine sediment. Its marine origin is responsible for a relative high organic matter content. The organic matter content is certainly not a homogeneous property for the complete Boom Clay layer. The absorbency measured at 280 nm varies between 1.1 and 7.4. The measured TOC values (in mg C/L) are between 41.3 and 144.

6. Ionic composition of the EG/BS clay water

The ionic composition of the EG/BS clay water is given in Table 1. The reported values are calculated from 11 samples except for SO_4^{2-} , Br and HPO_4^{2-} . In section 7, the ionic composition of EG/BS clay water will be compared with other piezometers to see whether the EG/BS water can be used as a "model clay water" for Boom Clay.

Table 1: Mean composition of EG/BS *in situ* Boom Clay porewater

Element	Mean ^{a)} (ppm)	95 % Confidence Interval		Standard deviation (ppm)
		Lower limit (ppm)	Upper limit (ppm)	
F	3.6	3.3	3.9	0.5
Cl	27	25	29	3
SO ₄ ²⁻	0.2	0	0.6	0.1
Br	0.49	0.45	0.52	0.02
HPO ₄ ²⁻	3.8	3.4	4.3	0.2
HCO ₃ ⁻	828	774	882	34
B	7.5	7.3	7.8	0.3
Na	408	403	413	7
Mg	2.9	2.7	3.1	0.3
Al	0.08	0.05	0.11	0.05
Si ^{b)}	5	0	9	6
K	11	8	13	3
Ca	4.0	3.8	4.3	0.3
Fe	0.9	0.8	1.0	0.2

^{a)} Mean value of following clay waters:

EG/BS.23.10.96;30.10.96;02.09.96;13.06.96;27.06.96;10.05.96;02.04.96;22.11.96;02.12.96;10.01.97;21.01.97

^{b)} Excluding two outliers: mean = 1.9 ppm Si; 95% confidence interval = [1.8; 2.06] ppm Si; standard deviation = 0.2 ppm Si

7. Comparison with other Boom Clay *in situ* porewater chemistry

The ionic compositions of other Boom Clay piezometers are given in Table 2.

Table 2: Ionic composition of *in situ* porewater of different piezometers

Element (ppm)	R11-32-W ^{a)}	R13-top-W ^{a)}	R15-top-W ^{a)}	SSE ^{b)}	SSW ^{b)}	Arch2-15m ^{a)}
F	2.71	1.99	2.43	n.d.	n.d.	2.86
Cl	22.3	18.5	21.7	47	36.7	23.9
SO ₄ ²⁻	0.68	0.39	0.2	12	14.3	0.53
Br	0.5	0.42	0.44	n.d.	n.d.	0.59
HPO ₄ ²⁻	1.37	0.42	0.61	n.d.	n.d.	0.9
HCO ₃ ⁻	574.4	782.8	813.3	773	927	n.d.
B	8.24	7.29	6.96	n.d.	n.d.	7.3
Na	323	239	326	345	405	387
Mg	2.08	1.32	2.83	1.99	2.61	4.1
Al	0.02	0.024	0.019	n.d.	n.d.	-
Si	6.25	5.19	5.61	5.13	4.26	6.7
K	22.9	9.75	9.71	8.4	11.1	11
Ca	3.01	2.55	3.79	5.49	5.53	5.2
Fe	0.44	0.068	0.35	0.95	0.74	0.8

^{a)} These piezometers were sampled in autumn 1996.

^{b)} Henrion *et al.*, 1985

Generally, the concentration of the major cations in porewater from piezometers, other than the EG/BS piezometer, are situated outside the 95 % confidence interval around the mean value for the EG/BS porewater. The difference with the EG/BS porewater however is small except for a few cases:

- The Na concentration of the EG/BS water is higher than all the other waters, except for the SSW, which is also a piezometer in contact with the Silty Layer.
- The sulphate concentration of SSE and SSW is much higher than the other clay waters. Most probably SSE and SSW clay waters were oxidised at the time of sampling. These numbers are not representative for the Boom Clay water.
- The K concentration of R11-32-W is much higher. This may be due to a measurement failure. In the EG/BS water, one of eleven analyses was also higher.
- The HCO_3^- of R11-32-W is much lower than for the other waters. This water has also a very small organic carbon content. Probably, this piezometer is not a good reference for the Boom Clay water.

8. Conclusions

- Considering the ionic composition, EG/BS clay water is, with the exception of Na, a good reference model water for the Boom Clay. This conclusion must be tested in the future, when more measurements of other piezometers are available.
- Considering the pH (~9.5) and considering the partial pressure of CO_2 ($10^{-3.72}$ atm), EG/BS is not a good reference model water for the Boom Clay. Whenever pH and CO_3^{2-} complexes are important in the experiment for which clay water is necessary, these parameters should be controlled in the EG/BS water.

9. Acknowledgements

A. Fonteyne, M. Van Gompel and L. Van Ravestyn are acknowledged for sampling the piezometers.

10. Bibliography

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