

Modelling boom clay formation porewater chemistry: ion exchange versus dissolution precipitation mechanisms

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Introduction

The main objectives of the ANDRA/CCE study presented here is understanding how water in contact with a clay formation acquires its chemistry. The knowledge of the different processes involved should help determine the major parameters that are needed to achieve geochemical modelling. Several organisations (BGS, BRGM, CEA, CEN/SCK, CNRS, ERM and GRAM) are taking part in this project which is funded jointly by ANDRA and CEC. BRGM is more particularly in charge of modelling clay-water equilibria from the study of the mechanisms of solid- and fluid-phase interactions. The first results of this study are presented here.

Method and main results

The clay formation studied is the Boom Clay Formation, about 35 Ma old and about 100 m thick which is sited between two sandy aquifers (Rupelian and Anversian sands) at about 225 m depth. Clay samples have been taken out from the Underground Research Facility in Mol, Belgium, from horizontal cores drilled under anaerobic conditions in order to minimize oxidation of the clay samples by air.

Chemical analyses carried out on the clay samples have shown that they are remarkably homogeneous. Chemical data along with mineralogical determinations using X-Ray diffractometry, scanning and transmission analytical electron microscopy and electron microprobe analysis have allowed us back calculating the mean composition of the studied clay: quartz: 18.9 %, albite: 2.8 %, K-feldspar: 6.0 %, calcite: 1.0 %, dolomite: 0.9 %, siderite: 0.4 %, pyrite: 4.2 %, iron oxide: 2.7 %, titanium, manganese and phosphorus oxides making up respectively 1.0 %, 0.03 % and 0.1 %.

The clay fraction amounts to 57.4 % by weight from which kaolinite makes up 10.1 %, illite 16.7

%, illite-smectite mixed layers 28.5 % and chlorite 21%. Water content for these clays ranges between 18.0 and 22.0 % by weight of dry sample.

Cation exchange capacities (CEC) have been determined following three methods cobaltohexamine chloride, cesium chloride and ammonia acetate, which were applied on two kind of samples: oxidised and non-oxidised samples. The results obtained show that: 1. The most appropriate method for our study is the one using cobaltohexamine chloride, as, even if it is not perfect, it allows us to determine exchanged cations in addition to the bulk CEC. Cesium chloride exchange tends to under estimate the real CEC, as part of cesium remains trapped in clay. Ammonia acetate yielded over estimation of the bulk CEC along with an over estimation of exchangeable calcium and magnesium by formation of calcium and magnesium acetate complexes; 2. The values obtained by cobaltohexamine exchange are fairly homogeneous. For oxidised samples (either air dried or dried at 105°C in a drying cabinet) the CEC obtained amounts to 24 meq/100g dry rock and is very close to the sum of exchanged cations. For non-oxidised samples, a large discrepancy exists between the bulk CEC measured (about 30 meq/100g dry rock) and the sum of exchanged cations (18 meq/100g only, what is different from oxidised clay). This discrepancy can be attributed partly to an over estimation of the bulk CEC because cobaltohexamine is readily complexed by organic matter and in particular humic acid present in non-oxidised samples, and partly to the under estimation of the sum of exchanged cations (occurrence of about 5 meq/100g dry sediment of exchangeable protons).

From the whole set of experiments we conducted, we can consider that the average CEC for this clay is 24.0 meq/100g dry sediment. For non-oxidised sediments, concentration of exchangeable sodium, potassium, calcium, magnesium and protons averages respectively 8.7, 2.3, 3.8, 3.7 and 5.5 meq/100g dry rock.

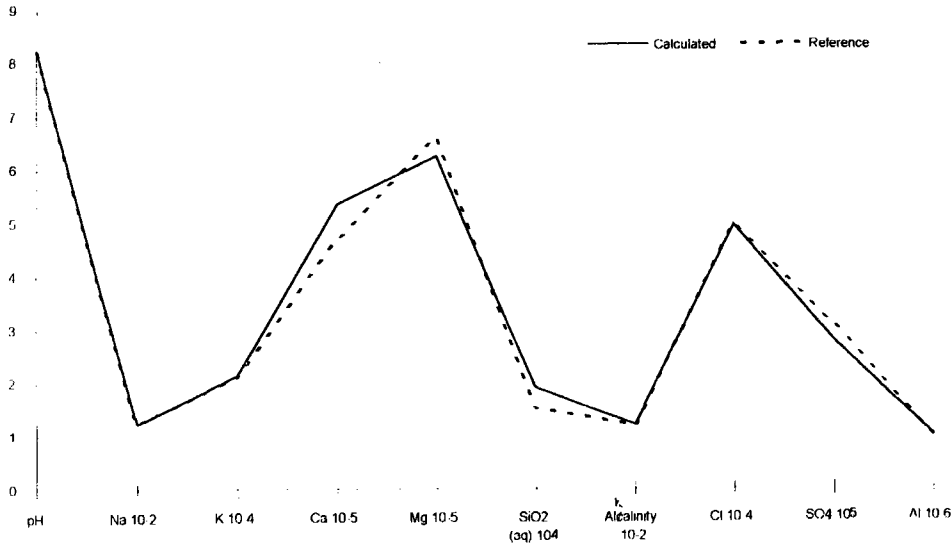


FIG. 1. Comparison between calculated water and reference water for the Boom Clay Formation.

Modelling

In order to model the clay-water system, we initially excluded the oxidised samples and their interstitial fluids as they result from external perturbation and can not be considered as representative of the original system. Interstitial fluid from non-oxidised fluid is essentially bicarbonated and sodic, whereas fluid from oxidised clay becomes sulphated and sodic, with much larger sodium concentrations than in non-oxidised fluids and pH possibly as low as 3. The chemical composition of fluids obtained from piezometers specially equipped for anaerobic sampling is considered as representative of non-oxidised clay fluids. The reference composition for major elements and aluminum used for modelling was obtained by statistical treatment of 15 analyses. The pH value has been adjusted to 8.20, which is the value measured in situ by means of a specific optic fibre (CEA, France). Eh (-310 mV) has been determined during the CERBERUS test (SCK/CEN).

Fluid chemistry has been calculated assuming

chloride concentration, carbon dioxide partial pressure and redox potential, and from equilibria between minerals and water. As for the control of sodium and potassium, two pathways can be followed:

1. A first possibility is to rely on the ion exchange experiments and apply the Vanselow's theory on ion exchange. In this case, a very good agreement is obtained between the calculated chemistry and the analytical determinations.

2. A second possibility is to calculate the equilibrium constants for clay mineral solid-solution such as Na-montmorillonite and illite and dissolved species. A good agreement between calculated and measured chemical compositions is hard to obtain that way.

Both methods are presented and discussed and it is demonstrated that the first one seems to be much more reliable and ready to use than the second one. Hence, we suggest that ion exchange mechanisms are dominant by far over clay mineral dissolution-precipitation to explain present day interstitial fluid chemistry in the Boom Clay Formation.