Geochemical Processes at the Carbon Steel/Bentonite Interface in Repository Conditions

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INTRODUCTION

The Deep Geological Repository (DGR) is currently the most accepted management option for the isolation of high level radioactive wastes. The DGR is based on a multibarrier system, which will limit releases of mobile radionuclides to the biosphere. In the Spanish design of the repository the spent fuel is encapsulated in canisters of carbon steel. The space between the canister and the host geological formation will be filled with bentonite buffer clay.

The effects of the reactions occurring in the canister/compacted bentonite interface should be understood for assessing the waste isolation. If canister failure due to corrosion occurs [1] the iron will be in contact with the bentonite affecting its properties, both in terms of the chemical evolution of the pore water and the properties of the bentonite. Iron precipitates can significantly change the properties of bentonite crucial for the migration of radionuclides such as porosity or sorption capacity. Ferrous ions can also pass through bentonite and precipitate as iron oxyhydroxides that can form pseudocolloids with radionuclides and quickly migrate in the host rock without sorption. But, the major effect of corrosion products will probably be the change of pH and E_h affecting the stability of the barrier and the release rate of radionuclides.

There are a number of studies on the corrosion of metals that could be used as canister [2], also studies on the iron-bentonite interaction [3], but not as many studies are focused to the iron-compacted bentonite interaction [4,5] and the associated mineralogical, chemical and physico-chemical transformations of the bentonite [6].

The experimental studies conducted by CIEMAT are focused on the iron canister corrosion products interaction with the bentonite system and are based on a series of short term and medium term experiments conceived at different scales, from conventional laboratory experiments and experiments in cylindrical cells, to those specifically designed 3D mock up experiments, the so called "GAME (Geochemical Mock up experiments) scale."

The experiments proposed in the context of the NF-PRO project (which is focused on understanding physical and numerical modelling of the key processes in the Near-Field, and their coupling, for different host rocks and repository strategies) have two main objectives: the study of the corrosion products generated in the canister/bentonite interface at the repository conditions, and to determine how the corrosion affects the properties of the bentonite. This paper describes the first tests performed to reach the objectives proposed and presents the results on the analyses of the corrosion products from carbon steel in contact with bentonite for a period of six months and one year subjected to heating and hydration.

EXPERIMENT

The tests were performed in hermetic cells. These cells consist on a compacted block of FEBEX ("Full scale engineered barriers experiment for a deep geological repository for high-

level radioactive waste in crystalline host rock") bentonite (Cortijo de Archidona deposit, Spain) that is hydrated on the top while a thermal gradient is applied from the bottom, where the bentonite block is in contact with a layer of carbon steel shavings or iron powder. In order to compare the influence of hydrating solution, time, temperature and the effect of oxic or anoxic conditions on geochemical processes associated to corrosion phenomena, six experiments were prepared. Five small cells (Figure 1) were assembled. The experimental conditions are shown in the section of results. Besides, another cell with a different design was used for an experiment in room conditions. In it, a piece of galvanized steel was sandwiched in a stainless steel mesh (Fig.2). This galvanic couple cause the almost complete dissolution of galvanized steel. This experiment was designed in order to study changes in porosity, permeability and other physical and chemical parameters that could be affected by the migration/precipitation of iron corrosion products in the bentonite block in the most aggressive conditions.

Corrosion products and bentonite were analyzed by XRD, FTIR and Raman spectroscopy, SEM-EDS, TGA and RBS. For swelling capacity measures, oedometers were used.

RESULTS AND DISCUSSION

The results obtained in these tests and the experimental conditions at which they were performed are shown in Table 1. The experimental conditions were chosen to study the influence of time, the amount of oxygen, and the type of steel. In all cases, lepidocrocite is present in the corrosion products layer together with goethite. For the small cells in which C-steel shavings were used, the iron oxyhydroxide layer was coating the bentonite surface in contact with the metal. This layer was porous and full of cracks, probably due to the stresses generated at the interface as a consequence of heating and hydration of bentonite. When bentonite gets hydrated it swells. However, the corrosion products layer cannot expand as much as the clay, so the stresses generated at this interface are released by the formation of cracks. These cracks are common to all cases, either at high temperature or room conditions.

The corrosion products seem to follow a sequence from bentonite to the steel shavings or the Fe powder. Iron oxyhydroxide or Fe(II)/Fe(III) hydroxide is coating the bentonite surface. These corrosion products are typical from an electrochemical corrosion process. Magnetite is below this layer in all the cells placed in an anoxic atmosphere. What should be elucidated now is if magnetite is generated as a consequence of the transformation of lepidocrocite or ferrous hydroxide or if it is formed by direct oxidation of metal during the saturation phase of the clay barrier.
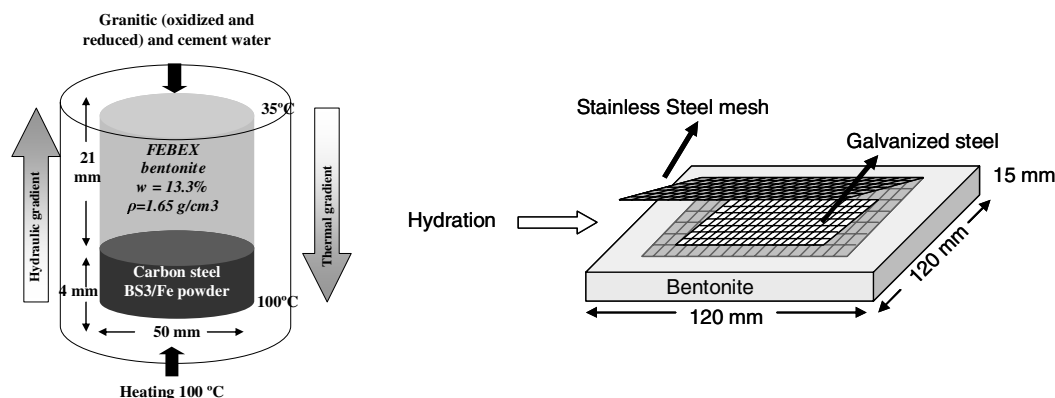
Figure 1. Scheme of the cylindrical cells used (small cells) and the experiment conducted under oxic conditions.

Table I. Corrosion products as a function of experimental conditions.

		Repository conditions			Oxic conditions
Fe source		Carbon steel (cell 1,2, 3)	Fe powder (cell 4)	Fe powder (cell 5)	Galvanized steel (cell 6)
Hydration		Granitic (oxidized and reduced) water Concrete water	Reduced granitic water	Reduced granitic water	Deionized water
Time		1 year	6 months	6 months	2 years
Temperature		100ºC	100ºC	25ºC	25ºC
Corrosion products	**Coating bentonite**	Lepidocrocite	Fe(II)/Fe(III) hydroxide Lepidocrocite	Lepidocrocite	Lepidocrocite
	Steel / Fe	Magnetite (Main corrosion product) Siderite (traces)			Lepidocrocite Siderite

Geochemical processes

The precipitation of salts (chlorides and carbonates) has been observed near the heater. In some areas the chloride content is up to 10% (atomic). This fact must be regarded, as a high concentration of chloride can induce localized corrosion processes. In cells 1-5, no chemical alteration of bentonite has been seen (fig 2A). XRD analyses have shown the formation of new iron rich phases in cells 1, 2 and 3. This could mean that time and temperature is required, as these phases have not been found at shorter time.

In cell 4, the colour of bentonite after the experiment was different from the original one. The first 7 millimetres (from the Fe/clay interface) of the bentonite block turned dark green and

after its exposure to air for a few minutes, it recovered its original colour. The cross-sectional analysis performed to the bentonite block does not show an appreciable increase of the Fe content in this area or the existence of green rust-like precipitates. Powder XRD analyses for the "green bentonite" show that d_{001} reflection shifted to higher d-spaces, but the d_{060} did not change its position and was found at 62° (1.49 Å), which indicates that montmorillonite has not been transformed into another mineral phase (fig.2B). Mössbauer analysis is going to be conducted in order to establish changes in the redox behaviour of the bentonite.
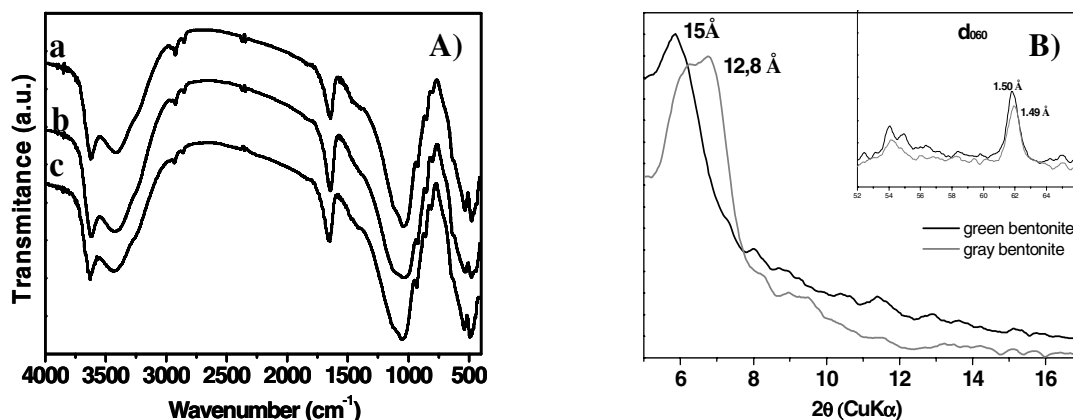

Figure 2. **A)** FTIR analysis of bentonite samples taken at different heights in the bentonite block (cell 2): a) near the heater, b) half-height, c) hydration zone. **B)** X-ray diffraction pattern of the "green bentonite" and the "gray bentonite."

The occurrence of iron oxyhydroxides in the walls and at the opposite surface to hydration in the cells show the migration of corrosion products colloids through the bentonite block. This fact, as well as the bentonite change of colour [6], has already been reported by Idemitsu [4,5]. It is important to point out that corrosion products can have a direct effect on transport of radionuclides as they can form colloids or pseudocolloids with radionuclides and quickly migrate in the host rock without sorption.

Cell under oxic conditions

In figure 3, some SEM images from the bentonite/steel interface are shown. In them a thin FeOOH layer seems to cover the bentonite surface. It is porous and full of cracks probably because of the stresses generated at the interface due to swelling of bentonite. In this experiment, most of the iron oxyhydroxide generated during the corrosion process has migrated through the bentonite block. Porosity, permeability, swelling capacity and other physical and chemical parameters can be affected by the migration/precipitation of iron corrosion products. Swelling capacity does not seem to be greatly affected by the migration of iron oxyhydroxides colloids. Only a slight decrease in swelling capacity and humidity was observed when the amount of lepidocrocite colloids increased.

Chemical analysis show some appreciable variations on Cation Exchange Capacity (CEC) values of bentonite as a function of the distance from the interface. The closer the sample was to the interface the lower CEC was.

It must be pointed out in this cell the precipitation of mixed Fe-Mg hydroxide at the interface, on the lepidocrocite layer. From this, it could be inferred that the chemical environment at the interface is controlling the availability of ferrous ions for diffusing through bentonite. In this case, despite the high amount of ferrous ions at the steel/bentonite interface because of the almost complete dissolution of galvanized steel, no new phases have been detected, probably because time and temperature are required.

Fe enrichment of clay seems to take place at the interface by cation exchange, occupancy of octahedral sheet sites, and probably by adsorption on surface groups of the clay. The EDS line analysis of the transversal cut of the bentonite block shows a decrease in the Fe content of clay as the distance from interface increases, however the iron contents found were low compare to the concentration of ferrous ions generated during the corrosion process. It seems that bentonite has a limit to host Fe in its lattice. Bakandritsos et al. reported that iron loadings higher than 5% do not produce new phases but the precipitation of iron clusters or iron oxides, since no more iron atoms could be hosted into the clay lattice as structural iron.
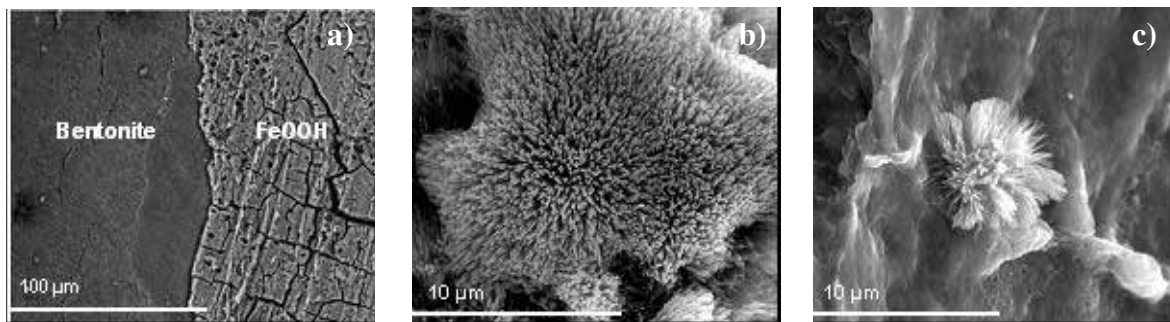

Figure 3. SEM images at the steel/bentonite layer: a) FeOOH layer coating bentonite surface; b and c) Fe-Mg hydroxides precipitated on FeOOH.

CONCLUSIONS

According to the preliminary results obtained from these experiments, montmorillonite does not seem to undergo any important mineral tranformation and its chemical and physical properties have not been affected significantly by the precipitation of corrosion products.

Further work must be conducted in order to elucidate the nature and possible tranformation of corrosion products of the metal canister and its impact on the stability of the clay barrier. So, medium to long-term experiments will give additional information on mineralogical and physical modifications of the clay barrier.

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