CHARACTERISATION AND MODELLING OF PHYSICO-CHEMICAL DEGRADATION OF CEMENT-BASED MATERIALS USED IN OIL WELLS

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ABSTRACT
Cement-based materials are used in oil and gas industry for cementing oil wells. The main role of the cement sheath is to permanently isolate all subsurface formations penetrated by the well. Long-term durability of cement-based materials used in oil wells is a major concern for oil and gas industry. Therefore, understanding of physico-chemical processes leading to cement degradation is a priority. In this study, we are presenting characterisation of chemical and physical properties for cement pastes exposed to leaching tests, and the modelling of these changes with a reactive transport model, HYTEC. The leached samples were cured with two different procedures aimed at reproducing the two different boundary conditions of the cement paste into the well. The results reported structural and chemical differences between the cement paste observed after the two types of curing, leading to a different behaviour after a three months leaching test in brine at 80°C. It was thus clearly demonstrated that curing conditions clearly influenced the degradation mode and kinetics during leaching. First simulations using the reactive transport code HYTEC with a simplified cement chemistry, allowed us nevertheless to reproduce some experimental results during cement pastes leaching, as mineralogical and physical changes.

INTRODUCTION
Cement-based materials are used in oil and gas industry for cementing oil wells [1]. The main role of the cement sheath is to permanently isolate all subsurface formations penetrated by the well. These geological formations can contain fluids which might induce physico-chemical alteration of the hardened cement paste. Consequently, some leakages of formation fluids from deep geological layers to shallow aquifers or to surface can occur through the altered cementitious matrix. Long-term durability of the cement-based materials is of paramount importance in this operation to guarantee the tightness of these wells. Moreover, this topic lies within the scope of new environmental stakes for oil industry, as CO2 geological storage. Many studies have been devoted to cement paste, mortar or concrete durability under conventional temperature and pressure conditions with the aim to understand the long term behaviour during nuclear waste storage [2]. However, the detailed mechanisms of cement degradation under downhole conditions are poorly documented [3].
The curing conditions of the cement paste used in durability studies appear to be of utmost importance [4,5,6]. The aim of the present work is to undertake different curing conditions for the cement pastes, understand its effect during leaching tests and to simulate the observed changes. First the boundary conditions experienced by the cement paste in the well were reproduced at the laboratory scale. Two curing conditions for the cement paste in the well have been taken into account. Indeed, the cement paste placed between geological formations and casing is altered by the fluids contained in the drilled rock formations as soon as it was put in place in the well, due to unequilibrium between pore solution and formation water. Another part of the cement sheath is just in contact with the casing and it is therefore protected against aggressive brine. Taking into account these boundary conditions, two curing modes have been implemented. Analyses revealed that curing conditions are a key factor influencing both the subsequent degradation mechanism and its kinetics. Our results pointed out the importance of calcite precipitation which plays a major role on fluid transport and thus on the rate of leaching. Experimental results were simulated using the reactive transport code HYTEC, imposing experimental domain (geometry of the leaching device and of the samples), physical and chemical environments (for the brine and the cement pastes) and boundary conditions (imposed flow during leaching tests). Results showed very accurately the fall of bulk mineral volume, assigned to portlandite dissolution and C-S-H decalcification, and the corresponding concentrations variation as a function of leaching duration. Porosity (considered as a variable parameter) for cement paste thus increased as degradation developed. The formation and the impact on the degradation of a calcite layer were also accurately simulated.

EXPERIMENTAL DETAILS AND MODELLING

Curing and leaching protocol
The anhydrous Class G CEMOIL Portland cement was obtained from Italcementi company. The Bogue composition [7] is given in the Table 1.

Table 1: Bogue composition for the Class G oilwell cement (wt. %)

<table>
<thead>
<tr>
<th>( C_3S )</th>
<th>( C_2S )</th>
<th>( C_4AF )</th>
<th>( C_3A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>62.2</td>
<td>12</td>
<td>12.2</td>
<td>2.2</td>
</tr>
</tbody>
</table>

The cement paste was made with a water/cement ratio \( w/c = 0.44 \). Before curing and leaching period, the specimens were hardened in cylindrical moulds (diameter = 40 mm, height = 70mm) and for 16 hours in pressurised cell curing chamber. The temperature and the pressure were 80 °C and \( 7 \times 10^6 \) Pa respectively. The pressurised autoclave was filled with water saturated with \( \text{Ca(OH)}_2 \), NaOH and KOH to prevent any ion diffusion of the cement interstitial solution.

Then the boundary conditions experienced by the hardened cement paste in the well were reproduced at the laboratory scale. After the initial hardening period, cement paste was cured during 1 month at 80 °C and at a pressure of \( 7 \times 10^6 \) Pa, by two curing modes.

- One half of the cement paste specimens was cut into cubic-shape (20 mm) and cured in a brine medium [3] (composition given in Table 2) representing the cement-geological formation interface (these samples were named “with exchange”). The cement monoliths
were placed on Teflon® grooved discs in a specific cell, filled with the brine, where pressure was imposed with N₂.

Table 2: Chemical composition of brine used for the study

<table>
<thead>
<tr>
<th>Species</th>
<th>H⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>HCO₃⁻</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrations (mol/kg)</td>
<td>4.13E-05</td>
<td>3.35E-01</td>
<td>3.29E-02</td>
<td>3.25E-03</td>
<td>1.83E-03</td>
<td>5.59E-03</td>
<td>3.69E-01</td>
<td>1.83E-03</td>
</tr>
</tbody>
</table>

- The second half of the specimens was placed directly in sealed containers to prevent any fluid exchange reproducing the cement-casing interface (samples named “without exchange”). All the pressurised cells were placed in an oven at 80 °C.

After the one-month curing period, cement paste specimens were leached 3 months at 80 °C by the brine taken for this study. The “with exchange” cubic samples were directly put in a four-litre High Density Polyethylene tank. Concerning the “without exchange” samples, 20 mm cubes were cut before being placed in a second tank. The cement cubes were maintained on a stainless steel mesh support; the two tanks were filled with the brine, and placed in the oven at 80 °C. The brine was renewed with a 0.5 litres per day flowrate thanks to a peristaltic pump. Leachant was collected separately in a ten-litre tank.

The software HYTEC
Modelling of cement leaching is the only way to predict the long term cement evolution [8,9]. HYTEC is a coupled reactive transport model developed by École Mines de Paris [10,11]. The numerical code takes into account geochemical heterogeneities and calculate physical parameters variations (e.g. porosity and diffusion coefficient) during mineralogical changes (dissolution/precipitation) leading mineral volume variations. HYTEC uses R2D2 that is a two-dimensional flow and transport module based on the representative elementary volume (REV) approach with finite volume calculation [12]. Chemical speciation is executed by the CHESS module [13]. This geochemical model is robust and allows chemical equilibrium state between different phases (aqueous and gaseous species, minerals, colloids etc.) within a system. Thermodynamic equilibrium state is solved by the basis component method according to an improved Newton–Raphson algorithm. CHESS is coupled with R2D2 with the aim of modelling species transport in the porous medium. Transport is coupled to chemistry according to the following equation [14,15]:

\[
\frac{\partial \omega e_i}{\partial t} = \nabla \cdot (Dd \nabla c_i - \omega \rho c_i U) - \frac{\partial \omega e_i}{\partial t}
\]

(1)

Where the dispersive/diffusive coefficient, \( Dd = D_e + \alpha U \). The term \( D_e \) is the effective diffusion coefficient, \( \alpha \) the dispersivity, \( U \) the Darcy velocity, \( \omega \) is the porosity, \( c_i \) and \( \bar{c}_i \) are the mobile and immobile concentrations of an element per unit volume of solution respectively and \( t \) is the time.

RESULTS AND DISCUSSIONS
Characterisation after the one-month curing period

The two curing conditions induced mineralogical and structural differences between the specimens. XRD, TGA and SEM analyses indicated that all the specimens contained both portlandite and C-S-H. Ettringite was not observed in these conditions [16], whereas hydrogrossular phase katoite was present in the cement paste [17]. AFm phase was not observed by XRD, may be due to very small crystals intermixed with C-S-H as shown by Taylor, 1997 [18]. It is important to highlight the difference between the two sets of specimens after one-month maturation. “Without exchange” samples were not altered whereas “with exchange” samples, cured one month in the brine, presented a 100µm-wide leached zone and a calcite surface layer. Diffraction spectra and TGA indicated that this degradation resulted in the partial dissolution of Portlandite and C-S-H decalcification. Indeed, the cement paste pore solution pH was about 13 whereas pH of the brine was close to 7.5. Thus ionic diffusion between the pore solution and the aggressive brine occurred. These concentration gradients within the pore solution created non-equilibrium conditions between the hydrate phases and this interstitial solution, so this equilibrium was recovered by dissolution and precipitation phenomena [19]. This is consistent with the hypothesis that the pore solution is over the overall volume, in local equilibrium with the solid phases. Partial decalcification of the “with exchange” cement pastes occurred to maintain calcium concentration of the pore solution. In addition, dissolved CO\textsubscript{2} in the brine can be also responsible of Portlandite dissolution, according to this reaction: \( \text{CO}_3^{2-} + \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \). This Portlandite carbonation is consistent with XRD and TGA analyses for the cement paste surface, which is constituted of calcite. This surface layer was already observed by several authors [20].

Characterisation after the three-months leaching period

After a three-months leaching test, “with exchange” specimens were highly-leached with a total degraded thickness reaching 7 mm, that corresponds to the portlandite dissolution front. SEM observations and XRD-TGA analyses allowed to clearly distinguish three different zones. A zone, situated in the centre of the cement monolith, containing all the principal phases (portlandite, C-S-H with C/S = 2, hydrogrossular). A first degraded zone, where portlandite was absent and C/S for C-S-H was about 1.5. Finally, a second degraded zone where C/S for C-S-H reached about 0.8 and portlandite was totally dissolved. These degraded zones were also characterised by a porosity increase. This phenomenon resulted in the decrease of the bulk mineral volume and enhancing fluid transport in the cement paste [21,22].

Concerning the “with exchange” samples, the calcite surface layer was further developed during leaching test, forming a crust at the monolith surface. Degraded zone was enlarged to reach about 250 µm, where portlandite was totally dissolved. This calcite layer allowed the reduction of leaching process [23] for these specimens, by forming a diffusion barrier.

Simulations results

The first approach of this study consisted to characterise physico-chemical modifications during oilwell cement leaching tests, with the aim of modelling these processes with the reactive transport model HYTEC. For the input data, cement paste is considers as completely hydrated.
Simulations results for three-months leaching are presented below. The main characteristics taken into account in the code HYTEC for the cement paste and the brine are presented in the table 2 and 3.

Table 3: Parameters used for simulations representing the two specimens after one-month curing

<table>
<thead>
<tr>
<th>Thickness degraded (mm)</th>
<th>Number of zones</th>
<th>Phases (% wt)</th>
<th>Sound zone</th>
<th>Degraded zone</th>
<th>Protective layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Without exchange&quot; samples</td>
<td>0</td>
<td>1</td>
<td>CH 17.0</td>
<td>C-S-H (1.8) 52.6</td>
<td>C-S-H (C/S) 2.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C-S-H (1.6) —</td>
<td>C-S-H (C/S) —</td>
<td>C-S-H (1.1) —</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C-S-H (C/S) —</td>
<td>CaCO3 3.0 —</td>
<td>CaCO3 3.0 —</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Afm 9.5 —</td>
<td>Hydrogarnet 10.0 —</td>
<td>Hydrogarnet 10.0 —</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Porosity (%) 28 —</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>&quot;With exchange&quot; samples</td>
<td>0.1</td>
<td>2</td>
<td>CH 17.0</td>
<td>C-S-H (1.8) 52.6</td>
<td>C-S-H (C/S) 2.0</td>
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<td></td>
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<td>Hydrogarnet 10.0 —</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Porosity (%) 30 —</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

A one-dimensional mesh for the cement domain had been chosen for the simulations. The cement paste domain had a 10 mm total thickness divided in 100 nodes. The external media, so the brine, was represented by a node where a constant concentration was imposed (Figure 1). Cement paste porosity and diffusion coefficient were considered as variable and the total simulation duration is 90 days.

![Figure 1: Geometry and mesh adopted for 1D simulations](image-url)
Modelling results are reported on graphs representing mineral phases profiles as a function of material depth. Figure 2a shows profiles for CH, AFm, C-S-H and Hydrogarnet after 3-months simulation. Portlandite dissolution front was situated about 4.5 mm, whereas leaching tests for the “without exchange” specimens showed that the total degraded thickness was about 7 mm. This front thickness is under-estimated and this can be explained by several reasons, like the fact that the simulations did not take account of CO2 dissolution in the brine involving portlandite dissolution.

Moreover, in this first degraded zone C-S-H (C/S = 1.8), AFm and Hydrogarnet concentrations decreased. C-S-H (1.8) dissolution led to the apparition of C-S-H with lower C/S (C/S = 1.6). We observed a second degraded zone (1 mm wide, according to experimental observations) where hydrogarnet and C-S-H (1.6) were totally dissolved. C-S-H with C/S = 1.1 was present in this area. A calcite crust was developed during leaching simulation. Indeed, calcium came from portlandite dissolution reacted with HCO3– in the brine, permitting local calcium saturation with calcium carbonate at the cement/brine interface [3]. This crust led silicon, calcium and aluminium accumulation in the interstitial solution, which involved an increase of the concentration of aluminium and silicon bearing phases like AFm and C-S-H near the edge of the cement paste. Figure 2b shows porosity variation along the profile, with an increase value between 4.5 mm and 1 mm where porosity value reached about 49%. This physical parameter decreased near the surface of the material because of calcite crust formation and re-precipitation of C-S-H (1.1) and AFm phases (porosity value is about 33 % between the surface and 1mm-depth). Theses observation are in good accordance with mercury porosity values (bout 39%) for the bulk degraded zones after leaching tests for the “without exchange” samples. So the mineralogical changes are accompanied by transport properties changes as porosity and simulations allowed the calculation of coefficient diffusion variations though a modified Archie law [24].

Concerning simulations for the “with exchange” cement pastes, a first mesh at the cement surface had been added in the input data, with 13% of Calcite. The thickness of this Calcite mesh was equal to 10 µm as it was observed by SEM after curing period for these specimens. More, a 100 µm-wide degraded zone was added according to observation after one-month-curing, where Portlandite and C-S-H (1.8) were partially dissolved. Figure 3a is an enlargement of the profile, and shows that the total degraded thickness was about 250 µm
(represented by the Portlandite dissolution.). C-S-H (1.8) further decreased but C-S-H with lower C/S ratio was absent because of a weak material degradation.

![Graph](image_url)

Figure 3: Modelling of chemical degradation for “with exchange” sample, mineral solid phases (a) and porosity (b) profiles as a function of the material depth

Calcite crust was further developed, and this diffusion barrier prevented the progression of cement paste degradation. More, figure 3b shows that porosity increased in the degraded zone, and decreased near the cement paste surface layer.

**CONCLUSIONS**

The boundary conditions experienced by the hardened cement paste in the well were reproduced at the laboratory scale. Two curing modes have been implemented at 80°C and 7×10⁶ Pa, then leaching tests with the brine were undertaken on the two sets of samples during three months at 80°C. Our results showed that the curing conditions are a key factor that clearly influences the degradation mechanism and its kinetics. It appears that a calcite layer plays a major role on fluid transport and thus on the rate of leaching. Modelling allowed us to reproduce some experimental observations. The results showed very accurately the fall of bulk mineral volume, assigned to portlandite dissolution and C-S-H decalcification, which concentrations are calculated as a function of leaching time. Porosity (considered as a variable parameter) for cement pastes thus increased as degradation developed. Second, the local precipitation of calcite, for the simulation of the “with exchange” samples, involved the use of a fine mesh on the edge of samples to account for the initial calcite layer, in order to obtain a good agreement with experiments.

**REFERENCES**


