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Evaluation of long-term behavior of concretes in high level waste repositories. An accelerated leaching test.

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The present work describes an accelerated leaching method that with a rapid process allows to develop and evaluate cements for use in a nuclear disposal, and the understanding of the long term effects. The method has been developed to study the stability of cementitious materials in contact with bentonite, to be used in high level radioactivity waste repositories. Nitric acid has been selected to simulate in an accelerated way the pH decreasing produced when concrete is in contact with groundwaters.

Evaluacion del comportamiento a largo plazo de hormigones en almacenamientos de residuos radiactivos de alta actividad

El presente trabajo describe un ensayo acelerado de lixiviación, que mediante un proceso rápido, permite desarrollar y evaluar cementos para su uso en instalaciones nucleares, y la comprensión de su comportamiento a largo plazo. El método se ha desarrollado para estudiar la estabilidad de materiales de base cemento, en contacto con bentonita, que serán utilizados en almacenamientos de resíduos radiactivos de alta actividad. Como agente lixiviante se seleccionó el ácido nítrico, con objeto de simular de forma acelerada, la disminución del pH que se produce cuando el hormigón entra en contacto con aguas subterráneas.

1. INTRODUCTION

The evolution of the microstructure of cementitious materials in contact with groundwaters, will vary depending of the type of cement used to produce concrete. Due to the long timescales involved in laboratory experiments using groundwaters, accelerated leaching tests, have to be used to qualify the different concretes for deep repositories, and to evaluate their long-term behaviour [1,2,3].

In realistic conditions of high level radioactive waste repositories, concrete durability is based on its interaction with clays and granitic groundwaters. In general groundwater is a very weakly mineralised solution containing diluted acids; however its exact composition is site-specific. In a deep repository scenario of flowing water, cement mass is chemically exposed mainly, to the pH of the incoming water that produces a progressive neutralisation of the alkaline nature of the cement paste, removing alkalis and dissolving portlandite and CSH gel.

Leaching test methods are in general used to estimate the leachability, leach rate and leaching conditions mechanisms of environmentally relevant components. However, for evaluation of sealing materials in high level waste repositories, it is necessary to investigate the mineral alteration of barriers such as concrete, and its interaction with other barriers (bentonite or granite), as well as to define the type of cement which produces an environment compatible with the surrounding materials.

The accelerated method proposed in this work, try to reproduce equilibrium or cuasi-equilibrium conditions, corresponding to different concrete degradation levels, in a short period of time.

2. DISSOLUTION-PRECIPITATION PHENOMENA OF CEMENT PASTES. ACID NEUTRALISATION TEST (ANT).

2.1. Leaching test procedure

The experimental procedure consists of a batch test; that is, a closed system [4, 5, 6]. Hydrated cement mixes are ground and sieved until a particle size less than 32 mm is obtained; then 10 g of this solid (S) are mixed with deionised water (L) in a ratio S/L=1, producing an homogeneous slurry. Accelerated tests are performed in these slurries by adding an acid (HNO$_3$, 1N), at a rate of 0.5 ml.min^{-1} with an automated titrator (Net Titrino 721 from Metrohm), and stirring the sample vigorously to favor continuous mixture of leachant and sample. In the case of nitric attack, a N$_2$ flow is maintained during the process to avoid carbonation. The evolution of pH is continuously recorded and liquid and solid phases are taken at different pHs corresponding to progressive degradation stages. The process of hydration is interrupted in each case by "freezing" the sample with acetone and ethanol; then samples are vacuum filtered through a 0.45 mm filter. Further analysis of the leachates and solid phases are carried out.

2.1. Materials

A Spanish cement (CEM I-SR according to the European Standard ENV 197-1) and two types of mineral additions (fly ash and silica fume) were used for this testing program. Cement pastes were fabricated with w/c=0.35 and they were hydrated during 7 days in sealed conditions (98% relative humidity and 20±2 ^{o}C). Formulations of pastes were: 100% CEM I-SR, 59% CEM I-SR + 41% FA, and 73% CEM I-SR + 7% FA + 20% SF.

2.2. Determinations and calculations

Chemical analysis results of the leachates were introduced in PHRQPITZ code using the database HATCHES [7], in order to calculate the thermodynamic status of such solutions; that is the saturation indexes of mineral phases.

Mid Infrared spectra of reference and degraded cement mixes, were obtained using a Nicolet Magna 750 Fourier transform IR spectrometer (FTIR) equipped with a DTGS detector. For each sample, 256 scans were recorded in the 4000-250 cm^{-1} spectral range with a resolution of 4 cm^{-1}. The spectra of all the samples were measured using the 12 mm diameter KBr pellets (0.1 mg of sample and 150 mg of KBr).

Solid state ^{27}Al M.A.S N.M.R was recorded at room temperature with a Varian VXR 300S spectrometer at 78.1393 MHz, with a spinning speed of 4 kHz in a double bearing 7mm ZrO_2 rotor. Spectra were accumulated using Bloch decay pulse sequences of $\Pi/8$ rad pulses and a recycle time of 1 s were used. NMR chemical shift of ^{27}Al were referenced to 1.0 M aqueous $Al(H_2O)_6^{3+}$.

3. RESULTS AND DISCUSSION

From thermodynamic calculations, it was considered that the potentially precipitating minerals will be those with the highest saturation indexes. In all cases solutions were oversaturated in different mineral phases; at pH=10, minerals with the higher saturation indexes were tobermorite and also chabazite; at pH=7 they were chabazite and Ca-Pzeolite. Results from some cement mixes are presented in Table 1.

In Fig. 1 the comparison of ^{27}Al MAS NMR spectra from a blended cement paste, before and after the leaching in HNO_3 medium, and at different pHs has been presented. ^{27}Al MAS NMR spectra of blended cement pastes including fly ash on their formulation, show the characteristic peaks of tetrahedral and octahedral aluminium [8]; where the observed chemical shifts are respectively centered about 55 ppm and –10 ppm. These spectra appear to be related to the aluminosilicates. The presence of tetrahedral and octahedral aluminium in the untreated sample, involves layer aluminosilicates or tectoaluminosilicates from fly ash.

TABLE 1. SATURATION INDEXES OF POTENTIALLY PRECIPITATING SOLID PHASES FOR CEMENT MIXTURES.

Mineral	Formula	pH	100% CEM I-SR	59% CEM I-SR 41% FA	73% CEM I-SR 7% FA 20% SF
Tobermorite	$Ca_5Si_6O17.5H_2O$	10	9.7657	9.1116	8.3644
Chabazite	$CaAl_2Si_4O12.6H_2O$	10	3.4057	3.1847	5.0327
Chabazite	$CaAl_2Si_4O12.6H_2O$	7	10.7107	9.6196	9.9802
CaP	$CaAl_2Si_{2.6}O_{9.2}.3.2H_2O$	7	7.5134	6.7377	6.9522

Brownmillerite (C_4AF), which remains unhydrated in cement paste, contains also some Al in tetrahedral sites. However, leaching increases the ratio Altetra/Alocta. This fact can be related with the incorporation of tetrahedral aluminium into the silica chains of the C-S-H gel [9, 10].

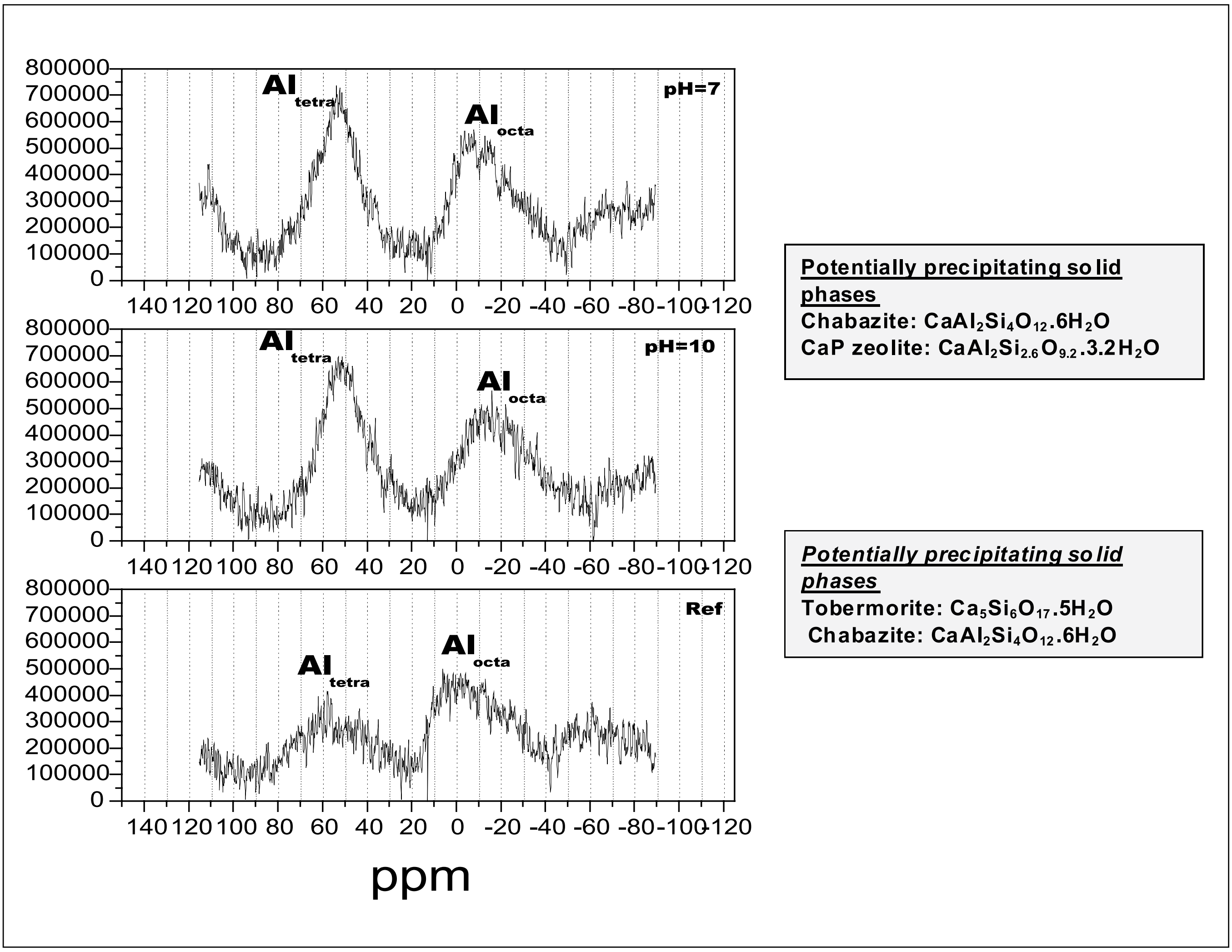

Figure 1. ^{27}Al MAS NMR spectra of a blended cement paste with fly ash

Figure 2 shows the mid-IR spectra in the lower frequencies; in this case the observed features provide useful information about Ca/Si ratio in CSH, silicate polymerisation, and the presence of TO_4 tetrahedra (T=Si or Al). Main information extracted from results is:

- For the CSH gels, the mid-IR bands occur at 950-1100, 810-830, 660-670, and 440-450 cm^{-1}. These mid-Ir bands change systematically with Ca/Si ratio in silicates which is also related with silicate polymerisation. The displacement of the band occurring at 976 cm^{-1}, to 1030 or 1080 cm^{-1}, in the case of leached samples, is due to an increasing in silicate polymerisation and a decreasing in Ca/Si ratio. The appearance of a shoulder at ~1200 cm^{-1} occurs when we have hydrated silicates with Ca/Si<0.7.

- The 660-670 cm^{-1} (Si-O-Si bending) band, increases in intensity for Ca/Si <0.88, consistent with an increasing in polymerisation.

- Bands in the range 400-500 cm^{-1} are due to deformation of TO_4 tetrahedra (T=Si or Al), and the increasing in intensity of this band when leaching proceeds, is also consistent with an increasing in polymerisation (more bridging TO_4 units linking dimers).

- Band at 1140 cm^{-1} can be attributed to ettringite which has completely disappeared in the sample leached until pH=7.

- Bands in the range 700-850 cm^{-1} can be attributed to the introduction of Al in tetrahedral coordination , which is significant for samples leached at pH=7, and consistent with previous results obtained by author.

- Bands at 875 and 320 cm^{-1}, are due to CO_3^{2-} groups in calcite.

Additionally, the disappearing of portlandite could be followed by the disappearing of the band at 3640 cm^{-1}, due to Ca-OH species in such compound.

Analyses of MID-IR spectra for cement pastes including mineral additions (59% CEM I-SR + 41% FA and 73% CEM I-SR + 7% FA + 20% SF), gave the same information. Small differences with the previously analysed data, could be attributed to initial differences in the Ca/Si ratio in silicates

Results demonstrated that the main processes occurred in leaching of samples based in Portland cement when exposed to a pH decreasing are:

- Alkalies release.
- Dissolution of portlandite.
- Decalcification of CSH gel.
- Silicate polymerisation forming a gel with a higher interlayer water content.
- Possible incorporation of tetrahedral aluminium in polymerised gel resulting in the formation of an alumino-silicate gel.

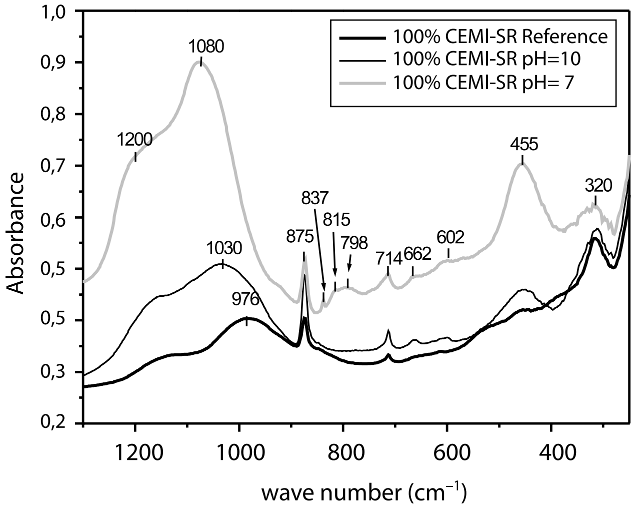

Figure 2. Mid-IR spectra of a 100% CEM I-SR cement paste. Silicate environments.

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