EVAPORATION TESTS IN PORTLAND MORTAR PROBES: ONGOING EXPERIMENTS AND NUMERICAL SIMULATIONS

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RESUMEN. Se están realizando, por un lado, ensayos de laboratorio con probetas de mortero con la finalidad de reproducir los procesos estacionales de lixiviación que se han observado en las paredes de hormigón de las celdas del repositorio de residuos radioactivos de baja actividad de El Cabril (Córdoba, España). Por otro lado, con el código de transporte reactivo multifase CODEBRIGHT, se realizan las simulaciones numéricas de los resultados experimentales. Esta estrategia sirve para comprobar la aplicabilidad del modelo geoquímico propuesto que contempla la disolución de los componentes mayoritarios del cemento Portland (portlandita, gel C-S-H, etc.) y la precipitación de minerales secundarios (sulfatos de Ca, calcita, etc.), siendo estos procesos similares a los que tienen lugar en la parte interna de las paredes de las celdas de El Cabril. Los ensayos de evaporación consisten en promover la circulación del agua de poro a través de una probeta de mortero Portland (OPC) que está parcialmente sumergida en agua de composición similar a la del agua subterránea de El Cabril. La evaporación en la parte superior induce el flujo de agua. Se mantienen constantes la temperatura, la humedad relativa y el nulo contenido de CO_2. Una vez finalizado el ensayo se examina la probeta mediante difracción de rayos X, microscopio óptico, SEM-EDS y fluorescencia de rayos X. A partir de los datos experimentales y numéricos se pretende: (1) determinar la variación de la relación Ca/Si de la fase C-S-H; (2) evaluar la variación mineralógica del cemento Portland (e.g., etringita, portlandita, etc.) y (3) cuantificar el efecto que produce en la porosidad del mortero a lo largo de la probeta. A partir de esta metodología, el modelo propuesto ha de utilizarse para calcular los cambios mineralógicos en las celdas de hormigón del repositorio.

ABSTRACT. Laboratory essays using mortar probes are being carried out to reproduce experimentally the seasonal leaching processes observed on the mortar walls of the cells of the low-level radioactive waste disposal facility at the El Cabril (Spain). Also, by means of the CODEBRIGHT code, numerical simulations are carried out to simulate the experimental results. This strategy is useful to check the applicability of the proposed geochemical model that contemplates dissolution of major phases of the mortar (portlandite, C-S-H gel, etc.) and precipitation of secondary phases (Ca-sulfate, Ca-carbonate, etc.) that in principle occur in the internal part of the concrete cell-walls at El Cabril facility. The evaporation essays consist of Portland mortar probes that are partially immersed in water with similar composition of the groundwater of El Cabril. At the top surface of the probe, evaporation takes places and circulation of porewater is promoted through the probe. Constant temperature, relative humidity and CO_2-free atmosphere is maintained. Once the essay is finished, the probe is examined by means of X-Ray diffraction, optical microscope, SEM-EDS and X-ray fluorescence. Based on the experimental and numerical data the objectives of the present study are: (1) to observe changes in the Ca/Si ratio of the C-S-H phase, (2) to evaluate changes in the cement-related phases (e.g., ettringite, portlandite, etc.) and (3) to quantify the effect that mineralogical changes exert on porosity along the test probe. With this approach, the model proposed should be useful to calculate the mineralogical changes that occur at the concrete walls of El Cabril facility.

1.- Introduction

The El Cabril disposal facility (Southern Spain) is a vault-type surface disposal repository for the storage of low-and intermediate-level nuclear waste. The concept of this multibarrier surface disposal system consists of waste packages (220 L drums) placed inside concrete containers (disposal unit). Mortar is injected into the containers to fill all available space between the drums. The containers are placed inside 24x10x10 m^3 concrete vaults. These vaults are situated in two storage platforms that have an infiltration control mains system.

Since the summer of 2003 water has been collected in the water collection system in some cells of El Cabril. The volume of flow shows a seasonal behaviour: water is accumulated in the second part of the summer and during a longer period of time in winter. Although the collected water does not have radioactive contaminants, this effect was a cause for concern because cement paste may be attacked by water with a low mineral content and approximately neutral pH (Faucon et al., 1998) promoting the destruction of the microstructure of the material (dissolution of soluble cement constituents such as calcium silicate hydrate C-S-H and calcium hydroxide), which affects the properties of the cement.

The most plausible hypothesis to account for the sources of this phenomenon is related to groundwater and the inflow mechanism, stating that the air gap between containers and vault walls produced seasonal differences of temperature of a few degrees, which provoked water vapour diffusion from the walls to the concrete containers in summertime or vice versa in winter (Saaltink et al., 2005; Zuloaga et al., 2006).

The El Cabril repository has a design life objective of longer than 300 years which is the time that low radioactive waste needs to reach the natural radioactivity level, but the water recollected in the collectors systems in the cells can change the properties of this mortar. Additionally, it is necessary to know how the evaporation of water in the walls of the cells affects the chemistry of mortar. To determine these effects a series of laboratory essays are being conducted to characterize the flux-evaporation effects. Likewise, a reactive transport model will be formulated which will include stationary flow in saturated medium with diffusion and chemical reactions in the matrix. The results of the calculations of water flow and the reaction in the mortar test tube will be compared with the observations.

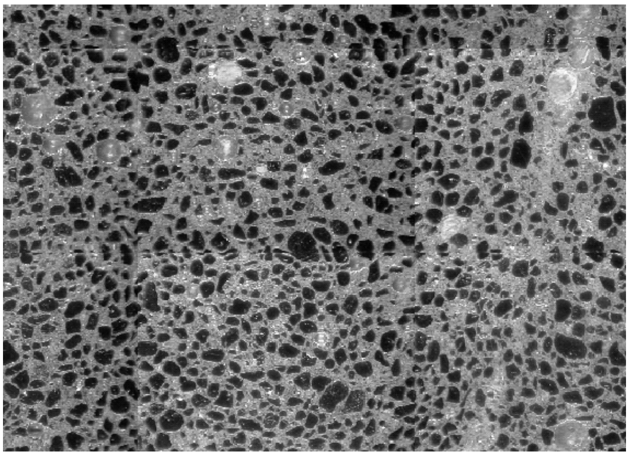

Fig. 2. Image that shows the homogenous distribution of Si-sand grains (dark grains) in the mortar matrix. The mean size of the grains is 500 μm.

2.- Materials and methods

2.1.- Material

The mortar probes were supplied by ENRESA. To ensure water circulation through the probe and surface evaporation at the top, the walls of the cylindrical probes were sealed and isolated with impermeable paint (Fig. 1).

Fig. 1. Image that shows the mortar probes (11 cm in height and 11 cm in diameter). The Probe walls are painted to prevent water evaporation through them and to guarantee evaporation through the top of the probe.

The characteristics and dosing of the mortar of the probes are those of El Cabril mortar (Table 1).

Table 1. Characteristics and dosing of the mortar probes.

Characteristics	Dimensions	11x11cm
	Cured type	Moisture room
	Total porosity (% v)	14.9
	Density (g mL^{-1})	2.0
Dosing (% wt.)	Cement I 42.5R/SR	20.0
	Water	13.7
	Sand "Mortise"	54.6
	Fly Ash "Eneco"	11.2
	Additive Rheobuild	2.4 L

A close examination of the mortar shows homogeneous dispersion of Si-sand grains (Fig. 2), indicating that the segregation did not take place.This involves that the water do not have preferential ways to go up through the test tube.

2.2.- Experimental design

The received probes were totally immersed in Milli-Q water under CO_2-free atmosphere. The initial weight increased until constant weight was achieved approximately after one month. At this point, porewater volume was 81.4 g, while the total pore volume of the probe was equivalent to 156.3 g. The probe was not completely saturated. The previously water-saturated mortar probe was then partially immersed for 24 days in an aqueous solution with composition similar to that of the groundwater in El Cabril site. To avoid carbonation through the test, a glove box was used to keep a CO_2-free atmosphere. Both glove boxes were equipped with two valves: one to allow entrance of N_2 gas from the supplying bottle and another to allow the exit of N_2 gas. The CO_2 concentration inside the boxes was always below 0.5 ppm. To guarantee a constant relative humidity of 31.5 % several beakers of 200 mL filled with supersaturated $MgCl \cdot 6H_2O$ solution were placed around the test probe (left glove box, Fig. 3). Thereafter, the top was irradiated with infrared light to ensure constant temperature (60 ˚C) at the surface and homogeneously distributed. Thus, a temperature gradient was generated from the irradiated surface of the specimen to the probe's bottom. Temperature, relative humidity and O_2% inside the glove box were constantly monitored.

As evaporation took place, water circulation from the bottom of the probe to the top was generated due to capillary suction. The amount of evaporated water was continuously replaced by water that was stored and equilibrated with N_2 to avoid CO_2 equilibration in the adjacent container (Fig. 3). The water tank was open and DDW water was permanently in contact with N_2 at atmospheric pressure. The flow of water from the reservoir was continuously monitored from weight loss using a balance.

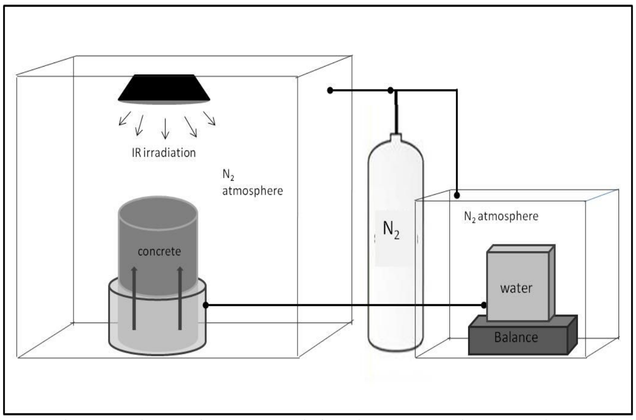

Fig. 3. The experimental setup used for the evaporation experiments in CO_2-free atmosphere (N_2) is shown schematically: the irradiated mortar probe is partially immersed in controlled volume of water. Evaporation is guaranteed to occur only at the probe top as the water container is sealed.

2.3.- Numerical simulations of the evaporation tests

The evaporation process in the mortar probe was modeled using the code CODEBRIGHT (Olivella et al., 1996). It allows simulations of multiphase flow and heat transport in unsaturated porous media.

The model consisted of a 1D domain discretized by means of a mesh of 50 nodes and 49 elements along the Z-axis, being more refined near the top of the surface where evaporation happened. The model considers unsaturated flow of liquid and gaseous water (vapor) and transport of heat as well as the interaction of these processes. Important parameters in unsaturated flow are the retention curve and relative permeability, which were taken from Chaparro (2010).

To represent the inflow of water at the bottom of the test tube a boundary condition of prescribed liquid pressure was used. To represent vapor loss and irradiation at the top surface the following boundary conditions for vapor and heat were used:

$$j_g^w = \left(\omega_g^w\right)^0 \gamma_g (P_g^0 - P_g) + \beta_g ((\rho_g \omega_g^w)^0 - (\rho_g \omega_g^w)) \qquad (1)$$

$$j_e = j_e^0 + \gamma_e \left(T^0 - T\right) \qquad (2)$$

where the superscript 0 stands for the prescribed values, j_g^w is the flux of water in gas phase (in mass per unit of surface per unit of time) and j_e the heat flux (in energy per unit of surface per unit of time), ω_g^w is the mass fraction of water in the gas, ρ_g is density of the gas, P_g is gas pressure, T is the temperature and γ_g, γ_e and β_g are parameters that represent the exchange of gas, vapor and heat between the probe and the ambient. The parameter $(\omega_g^w)^0$ represents the ambient vapor mass fraction and can be calculated from relative humidity ($(\omega_g^w)^0 = 2.385\cdot10^{-2}$ kg/kg). A sufficiently high value was given to γ_g, that practically prescribes the pressure of the gas at this top boundary ($P_g = P_g^0 = 0.101325$ MPa). The parameter β_g is a coefficient of vapor exchange between the probe and the ambient and was given a value of $8.1\cdot10^{-5}$ m/s. The parameter γ_e is a coefficient of heat exchange between the probe and the ambient and was given a value of 99 J/m^2/s/^{0}C. The parameter j_e^0 represents the heat flux due to radiation (j_e^0 = 175 J/m^2/s). Finally, T^0 represents the ambient temperature ($T^0 = 35^0$C).

3.- Preliminary results and Discussion

3.1.- Experimental data

Loss of water from the reservoir is shown in Fig. 4.

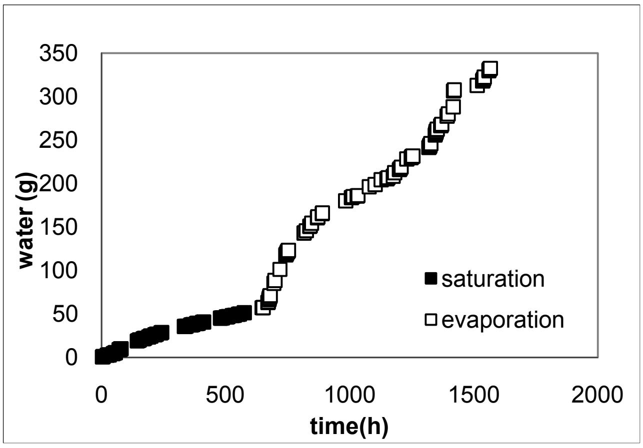

Fig. 4. Variation of water loss with time. Two stages are distinguished: (a) initial saturation of the probe for 24 days and (b) water evaporation until the end of the experiment.

Two stages are defined: at the first one, saturation of the probe is taking place through the probe's bottom for 24 days at room temperature, gaining 57 g of water. Saturation is assumed to be concluded when the amount of pore water reaches 138. 4 g. This value is close to 156.3 g that was calculated as total porosity. At this stage the estimated flow rate is 0.09 g h^{-1}. At the second stage the water loss through the top of the probe was promoted by water evaporation yielding faster flow rate (0.17 g h^{-1}). During all the experiment 275.25 g of water circulated through the test tube, 1.7 pore volumes. The experimental water flux was 6 x 10^{-6} kg m^{-2}s^{-1}.

3.2.- First approach of the CODEBRIGHT simulations.

The CODEBRIGHT code was used to obtain a temporal and spatial simulation of the evolution of the state variables and fluxes in the system for a period of 65 days. The parameters were fixed fitting temperature and water flow at the bottom and top of the test tube.

3.2.1. Temperature

Simulations show that irradiation at the top of the test tube by IR light originates a gradient across the mortar tube (Fig. 5).

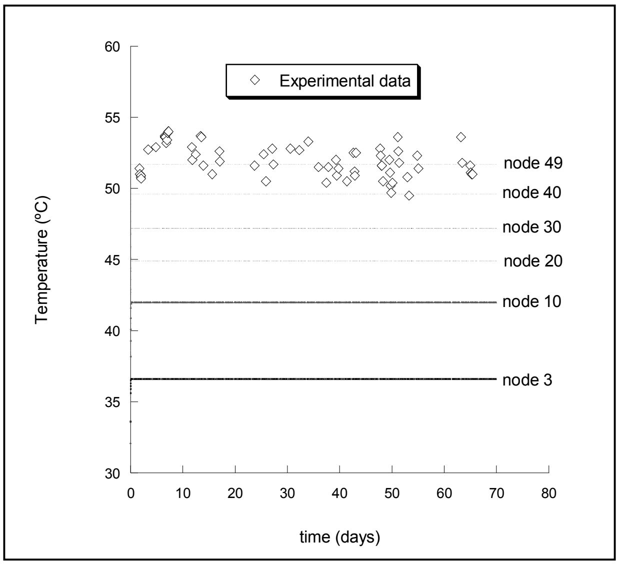

Fig. 5. Temperature variation with time in several nodes of the test tube. Rhombi represent the experimentally measured temperature at top of the test tube (node 49 in the model).

3.2.2. Saturation

The mortar tube is nearly saturated up to the forth element (7.85 cm). Saturation was reached after 1.22, 1.54, 2.32 d for the first two elements, elements 20 and 30, respectively. At the last element (40), that is closer to the irradiation source, saturation is 0.87, suggesting that evaporation happened in this area of the sample (3.15 cm on the top of the sample) (Fig.6).

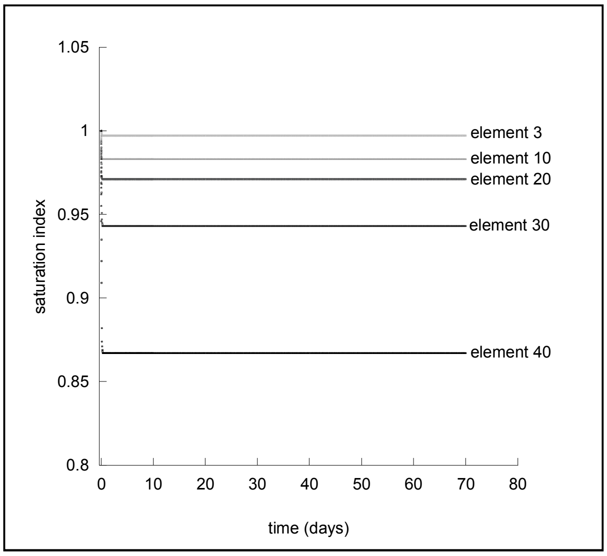

Fig. 6. Variation of saturation index with time in several elements of the test tube.

3.2.3. Water flux

The simulated water flux at the bottom of the sample is shown in Fig. 7. The model predicts a quasi constant and uniform input and output water flux of 6.3 x10^{-6} kg m^{-2} s^{-1}. This indicates that the water front advanced 0.55 mm per day, yielding 30 d as a residence time. This simulation is only preliminary although the simulated flux is close to the measured one. (6.0 x 10^{-6} kg m^{-2} s^{-1}).

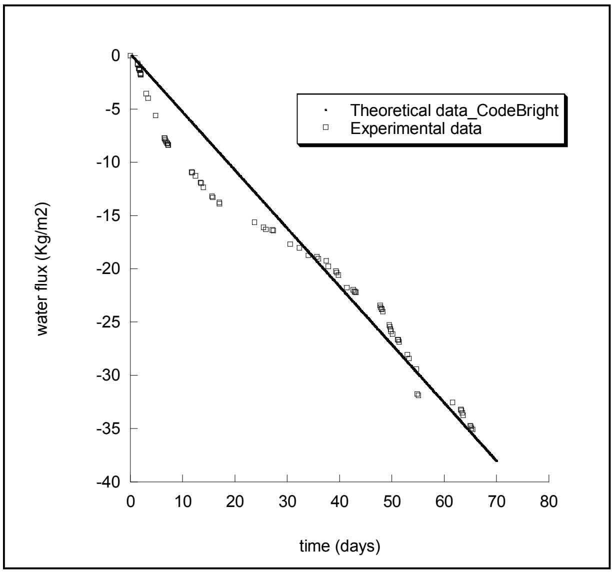

Fig. 7. Water-flux variation with time at the bottom of the test tube.

4.- Conclusions

Preliminary simulations of temperature and water flux show a good match with the respective experimental parameters. After this first approximation, examination of the microstructure changes at the evaporation zone (the top 3 cm) is going to be carried out.

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