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EFFECT OF THE TEMPERATURE ON THE LEACHING PERFORMANCE OF THE CEMENT-BASED IMMOBILIZATION SYSTEMS: SULFATE AND CHLORIDE BEHAVIOR

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ABSTRACT

The leaching in deionized water of sulfate and chloride ions from cement-based matrices of varying dosification (mixture of ordinary Portland cement and Boiling Water Reactor (BWR) evaporator concentrate solutions) were studied at the temperatures of 20°C and 40°C. The changes of the composition of both the extracted pore solution and the solid phases were characterized to see the possible related dissolution-precipitation processes of the cement hydrated aluminate and the competition established between both the sulfate and the chloride ions binding capacity. © *1997 Elsevier Science Ltd*

Introduction

Low and Medium Level Wastes (LLW) (MLW), from Boiling Water Reactor (BWR) contain, among others, a great concentration of sulfate and chloride ions, that could affect the durability of the cement-based materials in which they are immobilized. In Spain, those liquid radioactive wastes are being confined in matrices which are stored in reinforced concrete containers. A possible diffusion of such sulfate and chloride ions outside the matrices could, consequently, alter the stability of the different barriers: backfilling mortar and reinforced concrete containers.

Leaching data from such BWR-matrices in deionized water were previously reported (1-3). Guerrero et al. (1) studied the alkalinity of the BWR-matrix extracted pore solution and the changes caused by the leaching of alkalis. Goñi et al. (2) presented the capacity of the matrices earlier-mentioned for confining Cs^+ ion. Goñi et al. (3) studied the physical-mechanical properties of such BWR-matrices of varying cement dosification and the effect of the temperature (20°C and 40°C) on the Ca^{++} and OH^- ion leaching in deionized water. Fuhrmann et al. (4) investigated the influence of temperature on the leaching of the cement/sodium sulfate systems, but the authors did not study the leaching of sulfate ion.

In the present paper, with the same work methodology as that employed in (1-3), the effect of the temperature on the leaching of sulfate and chloride ions in deionized water from similar simulated BWR-matrices of varying cement dosification were studied by means of the American National Standard: ANSI/ANS 16.1-1986 (5). In addition, the composition changes of both the expressed pore solution and solid phase caused by the leaching attack were studied to see the possible related dissolution-precipitation processes of the cement hydrated aluminate and the competition established between both the sulfate and the chloride binding capacity. The pore solution was expressed by applying high mechanical pressure (6). The solid phase was characterized by X-Ray Diffraction (XRD) and Infrared Spectroscopy (IR).

Experimental Procedure

Ordinary Portland Cement (OPC) (Spanish type I-35) was used as a solidification agent of simulated BWR concentrate solution whose chemical compositions are given in Table 1. Matrices were fabricated at two BWR-solution to cement ratios: 0.65 and 0.53, which were called BWR-A and BWR-B, respectively. After mixing, samples were molded into cylinders (d = 5cm, h = 10 cm) and demolded after one day. The specimens were cured at 20°C and 100% RH for 28 days before the leaching process. The leachant was deionized water with a conductivity <5 µohms/cm, in which the specimens were immersed in individual plastic containers using a ratio of 10 cm between the volume of the leachant and the external geometric surface area of the specimen (196.35 cm^2). The experimental procedure was similar to that employed in previous works (1-3), in which details about the leaching test were given.

The pore solution was extracted by applying high mechanical pressure (500 MPa) (6). The chloride ion concentration was determined by titration against $AgNO_3$ 0.1N, by means of an Automatic Memotitrator Mettler DL40RC with potentiometric determination of the end point and that of sulfate by ion chromatography carried out with a Dionex 2000i/Sp instrument. XRD patterns were recorded on a Phillips PW 1730 diffractometer using a graphite monochromator and $CuK\alpha_1$ radiation. IR analyses were performed with a Perkin Elmer 305 instrument with a compressed air dryer accessory Balston P-E783; KBr pellets contained 0.5% of the sample.

TABLE 1

Chemical Composition of Starting Materials

OPC	**IL**	**IR**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**SO_3**	**Na_2O**	**K_2O**
(%)	2.40	2.49	17.9	6.50	2.73	60.8	2.80	3.10	0.67	0.99
BWR	**Na_2SO_4**	**NaH_2PO_4**	**Na_2HPO_4**	**$CaCl_2.6H_2O$**	**$FeCl_3.6H_2O$**	**pH**	**Density (g/cm^3)**			
(g/l)	95.64	29.92	59.88	8.76	38.64	5.5	1.16			

IL = ignition loss
IR = insoluble residue

Results and Discussion

Leaching Analysis. The Cl^- and $SO_4^=$cumulative fraction leached (CFL) from BWR-A and BWR-B matrices for the two temperatures, 20°C and 40°C, is plotted versus the square root of the leaching time in Fig. 1. The sulfate content from both the cement and the BWR-solution was taken as the reference concentration (45.3 and 44.3 g/Kg of matrix for A and B matrices, respectively). In the case of chloride, the reference concentration was the corresponding to the BWR solution (6.7 and 6.0 g/Kg of matrix for A and B matrices, respectively).

As seen, the CFL values increase considerably with the higher temperature, irrespective of both the Cl^- or $SO_4^=$ ions and the matrix dosification. Differences are clearly shown as a function of both the charge and size of ions. So, the CFL value for Cl^-, at the end of the experiment, was ~ 0.8 for BWR-A matrix at 40°C in comparison with 0.03 obtained for the $SO_4^=$ ion. Regarding the effect of the matrix dosification, the higher CFL values are obtained for the BWR-A matrices (of higher porosity).

In all of the cases the evolution of the CFL values with the square root of time follows a straight line (up to five days), which seems to show that by that time diffusion is the controlled leaching mechanism. A marked inflection is observed after five days in the CFL lines, principally for the $SO_4^=$ ion. That change of slope may be attributed to the formation of an external film on the sample surface which could impede the leaching process princi-

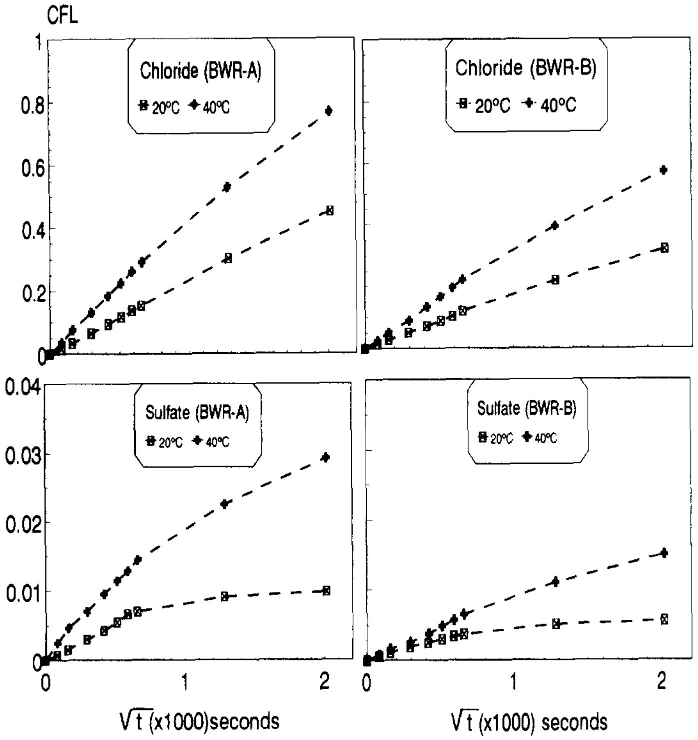

FIG. 1.
Cumulative Fraction Leached (CFL) versus time.

TABLE 2

Effective Diffusion Coefficients (cm^2/s) at 20°C and 40°C

	BWR-A				**BWR-B**			
$(\Delta t)_n$	**Cl^-**		**SO_4^{2-}**		**Cl^-**		**SO_4^{2-}**	
(days)	***20°C***	***40°C***	***20°C***	***40°C***	***20°C***	***40°C***	***20°C***	***40°C***
0.08	3.2e-08	1.5e-07	6.0e-11	6.9e-10	2.1e-08	6.9e-08	4.3e-11	7.1e-11
0.29	3.9e-08	2.1e-07	9.2e-11	6.3e-10	2.4e-08	9.8e-08	3.1e-11	8.5e-11
1.00	4.1e-08	1.2e-07	8.6e-11	2.3e-10	2.4e-08	6.1e-08	2.8e-11	4.8e-11
1.99	4.4e-08	1.6e-07	9.9e-11	3.4e-10	2.4e-08	1.0e-07	2.3e-11	6.9e-11
3.00	4.6e-08	1.7e-07	1.2e-10	3.3e-10	2.5e-08	1.1e-07	2.0e-11	1.2e-10
4.00	4.6e-08	1.8e-07	1.8e-10	2.8e-10	2.6e-08	1.0e-07	1.8e-11	9.0e-11
4.99	4.3e-08	1.8e-07	2.1e-11	4.1e-10	4.6e-08	1.0e-07	1.5e-11	8.4e-11
19.00	5.2e-08	1.9e-07	8.1e-12	1.3e-10	9.2e-08	9.7e-08	3.9e-12	4.2e-11
47.00	5.4e-08	2.2e-07	8.6e-13	6.6e-10	2.4e-08	9.6e-08	4.1e-13	2.2e-11

pally of divalent ions such as $Ca^{++}$and $SO_4^=$. As was pointed out by Serne (7), the formation of such film, which depends on the sample size and the length of the leaching experiment, affects the kinetic of the leaching process. Goñi et al. (3) observed, in a similar BWR-matrix, that the effective diffusion coefficient of Ca^{++} ion decreased one order of magnitude after five days of leaching.

The effective diffusion coefficients (D_e) for each leaching interval are given in Table 2. They have been calculated by the following expression:

$$D_e = \pi\,[(c_n/C_o)/(\Delta t)_n]^2\,[V/S]^2\,T$$

where: c_n is the activity or concentration released from the specimen during the n-th leaching interval; C_o is the total activity or concentration of a given ion at the beginning of the first leaching interval; $(\Delta t)_n$ is the duration of the n-th leaching interval in seconds; V is the volume of the specimen in cm^3; S is the geometric surface area of the specimen in cm^2 and T is

TABLE 3

Diffusion Data Obtained from Fig. 1

	BWR-A				**BWR-B**			
	Cl^-		**$SO_4^=$**		**Cl^-**		**$SO_4^=$**	
	20°C	**40°C**	**20°C**	**40°C**	**20°C**	**40°C**	**20°C**	**40°C**
(r)	0.9997	0.9999	0.998	0.998	0.999	0.999	0.998	0.999
slope	2.3e-04	4.4e-04	1.1e-05	2.1e-05	1.8e-04	3.4e-04	5.6e-06	9.8e-06
D_e(5 d)	4.2e-08	1.5e-07	9.5e-11	3.5e-10	2.6e-08	8.9e-08	2.5e-11	7.5e-11
D_e^*(5 d)	4.2e-08	1.7e-07	9.4e-11	4.2e-10	2.7e-08	9.1e-08	2.5e-11	8.1e-11

D_e^* average calculated from the abbreviated leaching test.

the cumulative leaching time representing the "mean time" of the n-th leaching interval for a semi-infinitive medium:

$$T = [1/2\,(t_n^{1/2} + t_{n-1}^{1/2})]^2$$

Generally, this way to calcule "D" is valid up to five days of interval leaching time (abbreviated test), where diffusion is the rate-determining mechanism. At this point the specimen acts like a semi-infinite medium. From five days, the specimens, generally, act like a finite medium, being the cumulative fraction leached higher than 20%, and other methods to calcule D must be used. So, for example a graphical method or interpolation, from which the parameter "G" is obtained, being in this case:

$$D_e = Gd^2/(\Delta t)_n$$

where: d is the diameter of the specimen in cm, and G an addimensional factor.

As shown in Table 2, D_e values for the $SO_4^=$ ion are, in general, three orders of magnitude lower than those of the Cl^- ion, irrespective of the temperature and matrix dosification. The effect of the temperature is more marked for the BWR-A matrix. After 47 days of leaching, D_e sulfate values decreased ~two orders of magnitude when the leaching temperature was 20°C. In contrast chloride D_e values were almost not affected. The sulfate D_e values decrease with the leaching time could be related to both the formation of the protector external film on the sample surface and the precipitation of sulfated compounds such as ettringite. Diffusion of chloride seems not affected by that external film, probably due to its lower ionic charge and ionic effective radius, and consequently, its lower binding capacity. To verify those hypothesis the pore solution and solid phase were characterized.

If diffusion is the control mechanism of leaching, the effective diffusion coefficients (D_e) can be also estimated from the slopes of Fig. 1 by applying (8):

$$CFL\,(V/S) = 2(D_e/\pi)^{0.5}\,t^{0.5}$$

where: V is the volume of the sample (196.5 cm^3), S is the external surface (196.5 cm^2), t is the cumulative leaching time in seconds, D_e is the effective diffusion coefficient in cm^2/s and CFL is the cumulative fraction leached ($\sum_{n=1}^{n=9} c_n / C_o$).

The correlation coefficients (r) of the regression equation obtained from the first lineal zone (up to five days) as well as the slopes and D_e coefficients are presented in Table 3. The average value determined from the leaching test (D_e^*) are also included. In general, a quite good concordance between D_e values, calculated from the two ways, is obtained.

Pore Solution Analysis. The percentages changes of chloride and sulfate ions dissolved in the pore solution because of the leaching attack are presented in Fig. 2. The percentages were calculated from the concentrations analyzed in the extracted pore solution, according to Diamond`s method (9).

The lower concentration of $SO_4^=$ in comparison with that of the Cl^- ion, at 0 days (before leaching), suggests that $SO_4^=$ is more easily combined with the solid phases. Particularly, the 15% and 13% of the total amount of $SO_4^=$ is dissolved in the pore solution, for BWR-A and B matrices, respectively whereas the 76% and 58% are dissolved for the Cl^- ion (see Fig. 2).

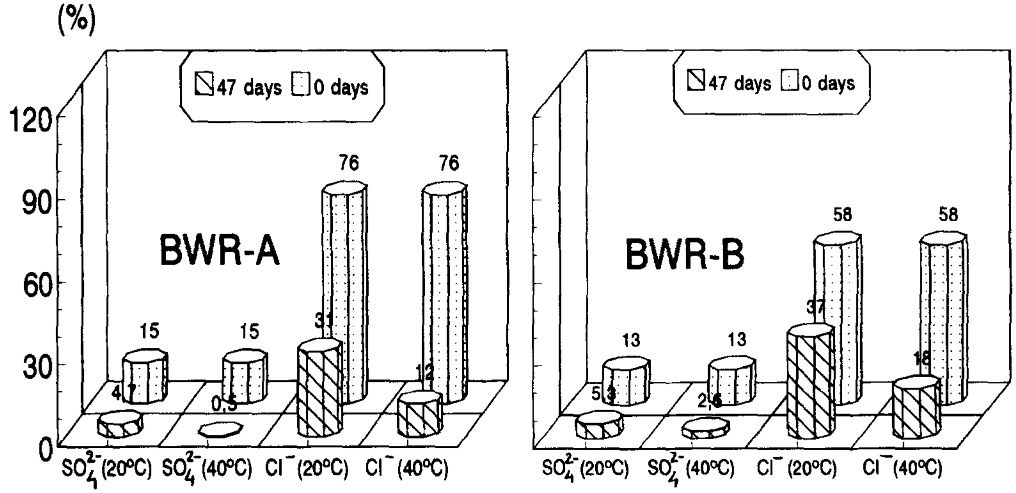

FIG. 2.
Percentage of ions dissolved in the pore solution.

This fact could be one of the factors which contributed to the different effective diffusion coefficient values obtained for these ions. The percentages after 47 days of leaching strongly decreased due to the ions are removed from the pore solution in the leach process.

From the comparison of the $SO_4^=$ and Cl^- percentage changes in the pore solution before and after the leaching with the corresponding cumulative fraction leached (CFL), some interesting hypothesis on mechanisms involved at later ages of leaching time could be established (Fig. 3). The dashed central zone represents equal values of CFL and pore solution data (given with a precision 10%).

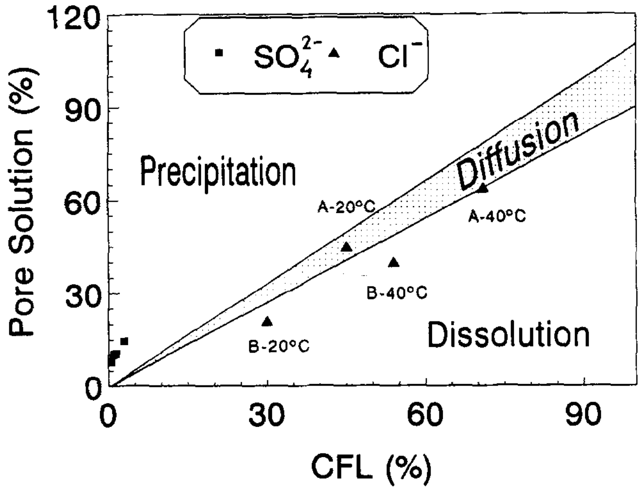

FIG. 3.
Pore solution percentage changes vs CFL values.

If diffusion is the rate determining mechanism of leaching, the percentage changes in the pore solution would be equal to the corresponding CFL values. That is the case of BWR-A matrix leached at 20°C during 47 days, where the cumulative fraction leached ($\Sigma c_n/C_o$) for the chloride ion has a value of 45%, and the difference in percentage, of that ion dissolved in the pore solution before and after the leaching process, is 45%. If precipitation or adsorption processes take place, pore solution data would be located over the dashed zone, as is the case of $SO_4^=$ ion (where its CFL for the BWR-A matrix leached at 20°C has a value of 0.98% and its percentage in the pore solution decreased ~ 10%). On the contrary, pore solution data located below the dashed zone would show the dissolution of the solid phase, as is the case of Cl^- ion (where its CFL for the BWR-A matrix leached at 20°C has a value of 71% and its percentage decreased in the pore solution ~ 64%).

The solid phase was characterized by XRD and IR analyses to verify the possible aforementioned hypothesis.

X-Ray Diffraction Analysis. The XRD results are presented in Figs. 4 and 5 for BWR-A and B matrices leached at 20°C and 40°C respectively. As shown, before leaching (0 days) the presence of Friedel's salt ($C_4ACl_2H_{10}$), is detected, in both matrices. No crystalline sulfated phases are present prior to leaching. The intensity of the Friedel's salt reflections decreased with the leaching time whereas ettringite reflections appeared more clearly for BWR-A matrix (see Fig. 4 and 5 (c)). That seems to suggest that Friedel's salt is dissolved during leaching and the $SO_4^=$ ion is combined as a non-well crystallized ettringite (the intensity of ettringite reflections is very low, especially in the case of BWR-B matrix).

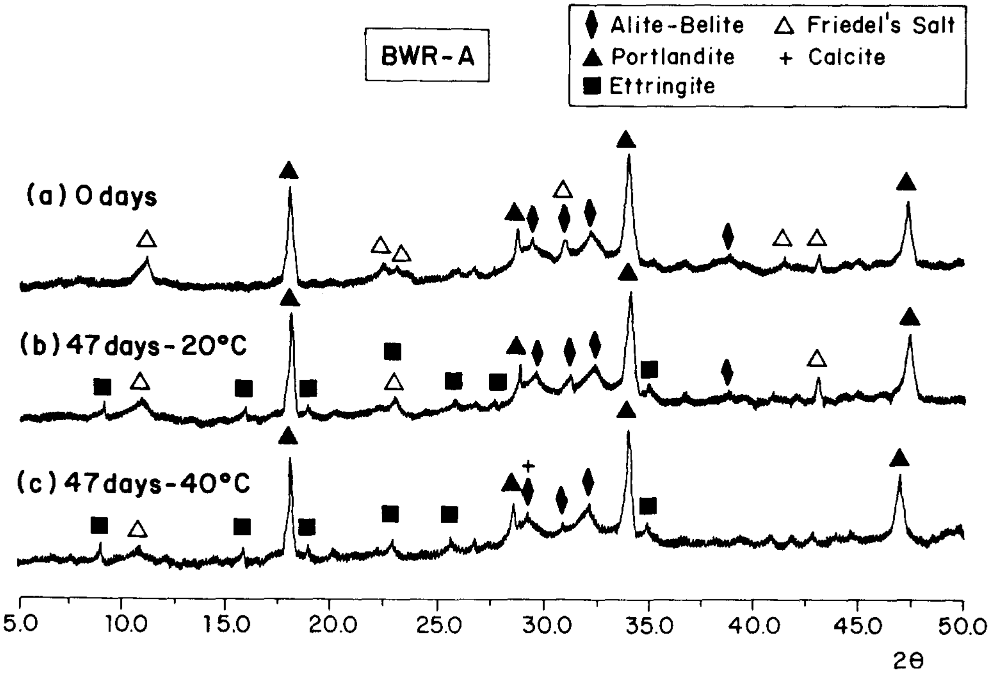

FIG. 4.
XRD results of BWR-A matrix.

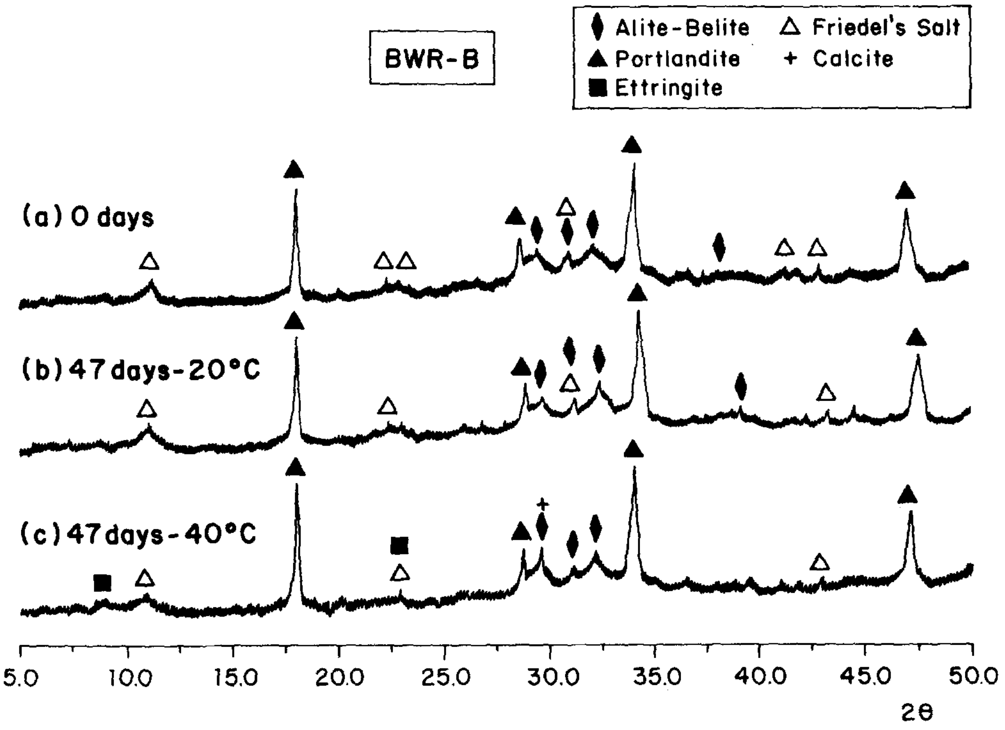

FIG. 5.
XRD results of BWR-B matrix.

Infrared Spectroscopic Analysis. As was earlier-mentioned the matrices were coated with a protector film which looks gel-like and that could impede the transport of bigger ion such as Ca^{++} and $SO_4^{=}$ outside the matrices. That could be one of the causes of the markedly slope change evidenced in Fig. 1. The characterization of that film by IR analysis is presented in Fig. 6 together with the internal part of the matrix before and after the leaching. As shown the IR spectra are quite similar. The main differences detected in the external film are:

The sharp band corresponding to the stretching vibration of the OH^- groups of portlandite at 3660 cm^{-1} disappeared and the relative intensity of the rest of the bands increased in the film region. Bands corresponding to the internal vibrations of the water molecules were detected: stretching vibrations at 3600-3400 cm^{-1} and the deformation vibrations at 1650-1620 cm^{-1}. The presence of $CO_3^{=}$ ion is evidenced for the strong absorptions in the lattice region 1530-1320 cm^{-1}: bands at 1480 and 1420 cm^{-1} (v_3), medium strength bands between 890 and 800 cm^{-1}: 880 cm^{-1} v_2. The intensity of these bands considerably increases in the spectrum of the external film.

In the 1300-400 cm^{-1} lattice region on this spectrum (c) several bands appeared which may be attributed to the $SO_4^{=}$ ions: the split absorption bands found in the range, 1210-1040 cm^{-1}, corresponding to v_3 vibration mode (1140 and 1050 cm^{-1}) and the weak absorption at 960 cm^{-1} (v_1) and 570, 450 cm^{-1} (v_2). As shown, the intensity of these bands is higher than the ones detected in the others spectra. Others ions such as phosphates and silicates which are present in the matrices could also show vibrations bands at those frequency ranges (10-12).

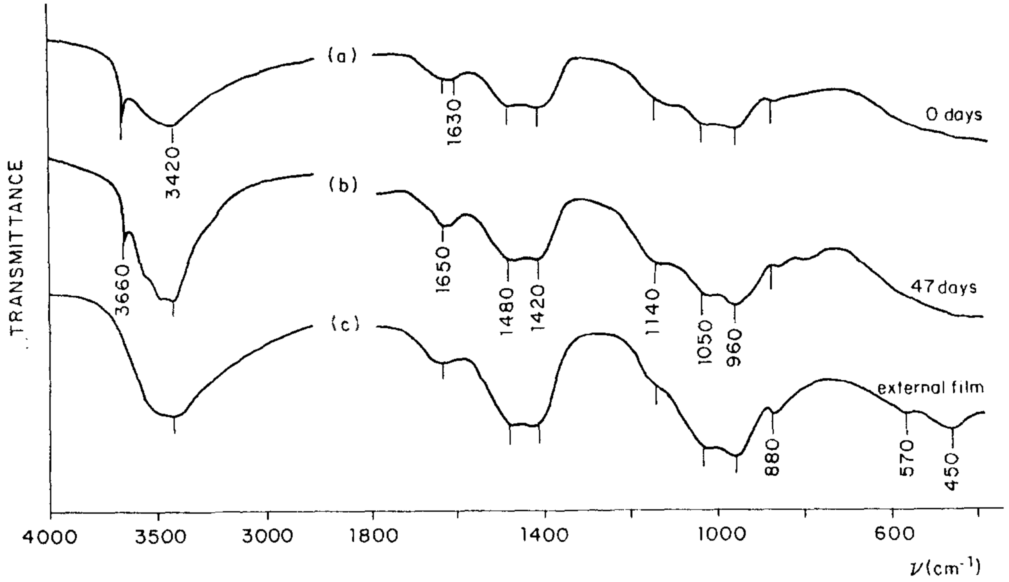

FIG. 6.
IR results of BWR-B matrix.

These data reveal that the $SO_4^{=}$ ion is precipitated on the external film as well as is combined with solid phase of the matrix impeding its leaching at later ages.

Conclusions

A great amount of the sulfate ion remains either combined with the solid phase of the BWR matrix or adsorbed on the surface of the external film which cover the samples during leaching. Consequently, the diffusion capacity of sulfate ion outside the matrices is markedly lower than that of chloride ion.

The high free-chloride content in the pore solution together with the dissolution of the Friedel's salt during the leaching favoured the chloride ion transport.

The effect of the temperature is clearly manifested by increasing ~3.6 times the effective diffusion coefficients (D_e) of both the sulfate and the chloride ion for the BWR-A matrix dosification and ~3.4 times for chloride and 3.0 times for sulfate in the case of the BWR-B dosification (of the lower porosity).

Irrespective of the temperature, the effect of the cement matrix dosification is also manifested by increasing the effective diffusion coefficients ~1.6 times for chloride and 3.8 times for sulfate ion in the case of the BWR-A matrix (of the higher porosity). Consequently the effect of the dosification is more marked for the sulfate ion.

The chloride content of the BWR matrices could be a more potential aggressive in comparison with sulfate ion because of its higher diffusion capacity. Therefore attention has to be paid from the point of view of the corrosion of metallic reinforcements of the concrete containers.

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