

Deterioration and Diffusion Studies of Radioactive Wastes from the Concrete Matrix by Dynamic Method

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Abstract: In designing radioactive waste repositories, it is necessary to predetermine the degree of cement performance change due to leaching degradation. Cement is a porous material and consists of solid phases in contact and in equilibrium with a pore water solution. The progress of degradation can be expressed in terms of water exchange cycles or speed of diffusion of ions in the pore solution. Cementitious materials are fundamentally unstable in water and will change properties with time. High pH conditions of aqueous solutions in a radioactive waste repository can be brought about by dissolution of cementitious materials. In order to clarify the mechanisms involved in maintaining this high pH for long time, the dissolution phenomena of cement hydrate was investigated. In the present research, leaching tests on powdered cement hydrates were conducted by changing the ratio of mass of leaching water to mass of cement hydrate Ordinary Portland cement hydrate was contacted with pour water and placed in a sealed bottle. After a predetermined period, the solid was separated from the solution. Calcium hydroxide is one of the main reaction products resulting from the hydration of Portland cement with water. It is also one of the more soluble phases found in hydrated cement systems. Study's the influence of calcium hydroxide dissolution and its effect under the dynamic leaching system. From the results of XRD analysis on the solid phase and the calcium concentration in the aqueous phase, it was confirmed that $\text{Ca}(\text{OH})_2$ was preferentially dissolved when the liquid/solid ratio was 30 to 35 %, and that C-S-H gel as well as $\text{Ca}(\text{OH})_2$ were dissolved when the liquid/solid ratio was 45% or larger. The crystalline phases were identified using X-ray diffraction. The leaching of ^{137}Cs was carried out according to the ANSI/ANS -16.1.

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Introduction

Concrete structures such as reservoirs, tanks, dams, water- supply pipes are attacked by soft water for a long time and which may result in concrete degradation as well as environmental problems. Similarly, radioactive waste facilities are designed to be placed underground 100m to 1,000m, where are underwater, and those are needed high durability for a long period over 1,000 years. Cement is considered to be an important component in low level waste (LLW) disposal systems. However, the long-term evolutions of its mechanical strength and its ability to confine radio nuclides have not yet been clarified, which has resulted in uncertainties in long-term repository performance assessment. Cement hydrates will be altered by dissolution of their minerals on contacts with groundwater: this is considered to be a major factor in changing various properties of cement hydrates. The chemical characteristics of pore water (pH, Eh, concentration of nuclides, etc.) dominated by dissolution of cement minerals are considered to influence surrounding environments such as the waste form, bentonite and rock.

Therefore, investigation of cement dissolution behavior is very important in assessing the long-term performance of the repository. The behavior of cement

dissolution has been studied by many researchers. [1-4] have modeled the cement dissolution behavior and calculated the long-term evolution of its composition in the aqueous phase. [5,6] studied hydrated cement and suggested that it dissolves by competitive reactions (leaching from the surface and diffusion inside), and that the phase and the structure of the hydrated minerals will change with the progress of dissolution.

Accordingly, in assessing the long-term performance of a cement barrier, it will be necessary to define the long-term alteration behavior of the cement hydrates. Recognizing the importance of clarifying change in cement hydrates associated with the progress of dissolution in the evaluation of solubility and chemical durability and in modeling cement alteration, dissolution tests of hydrated cement have been conducted. [7-9] X-ray powder diffraction (XRD) has been used to analyze the structure of inorganic minerals. However, as the crystallinity of hydrated calcium silicate gel ($\text{XC}\text{aO}-\text{YSiO}_2-\text{ZH}_2\text{O}$: hereafter C-S-H gel), a primary mineral of hydrated cement, is low, it was difficult to analyze the structure by XRD. While the change in structure due to dissolution is not clear, structural changes in C-S-H gel could affect the physical properties of cement hydrates. In order to assess the long-term barrier performance of cement

hydrates, analysis of the structure of C-S-H gel is a key issue.

Portland Cement is composed of four principal phases: alite (C_3S : $3CaO \cdot SiO_2$), belite (C_2S : $2CaO \cdot SiO_2$), a ferrite phase (C_4AF : $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$) and an aluminate phase (C_3A : $3CaO \cdot Al_2O_3$). The calcium silicate phase (alite and belite) accounts for 65 to 70 wt%. The hydration of the calcium silicate phase produces C-S-H gel and portlandite ($Ca(OH)_2$). C-S-H gel and $Ca(OH)_2$ were the main products of the hydration of the Portland cement. However, as the crystallinity of hydrated C-S-H gel is low, it was difficult to analyze the structure by XRD.

The objective of this study was to know how the cement changes both its chemical and physical properties over time and how it interacts with groundwater by used the dynamic leaching test. The concentrations of calcium and silica in the leachate were measured. The crystalline phases were identified using XRD. The leaching of ^{137}Cs was carried out according to the ANSI/ANS -16.1 [10]

Experimental procedure

1-Materials

Portland cement:

The tests were conducted using ordinary Portland cement which was kindly supplied from Suez Cement Co., Egypt, the measured Blain surface area was ~ 350 cm^2/kg . The chemical composition of the cement was presented in table (1) The XRD of cement is presented in fig.1n general, the major factors causing deterioration of cementations materials are water, corrosive components contained in water, carbon dioxide in the atmosphere, and heat. In repository, the concrete should be considered to be exposed to ground water containing small quantities of corrosive components, therefore, are considered to be the tow major factors for degradation of hydrated cement. The reaction is very slow due to the low diffusivity of ions through the pores in hardened cement paste. The dynamic test is to acceleration calcium (Ca), silica (Si). Specimen preparation a mortar mix of ordinary Portland cement mixed with ^{137}Cs were prepared at a different three water – cement ratio 0.35, 0.45 and 0.50. These mortars were cast in cylinder molds (2.24cm in diameter, 5 cm in height) for leaching test and curing in lab., at ambient temperature for four weeks.

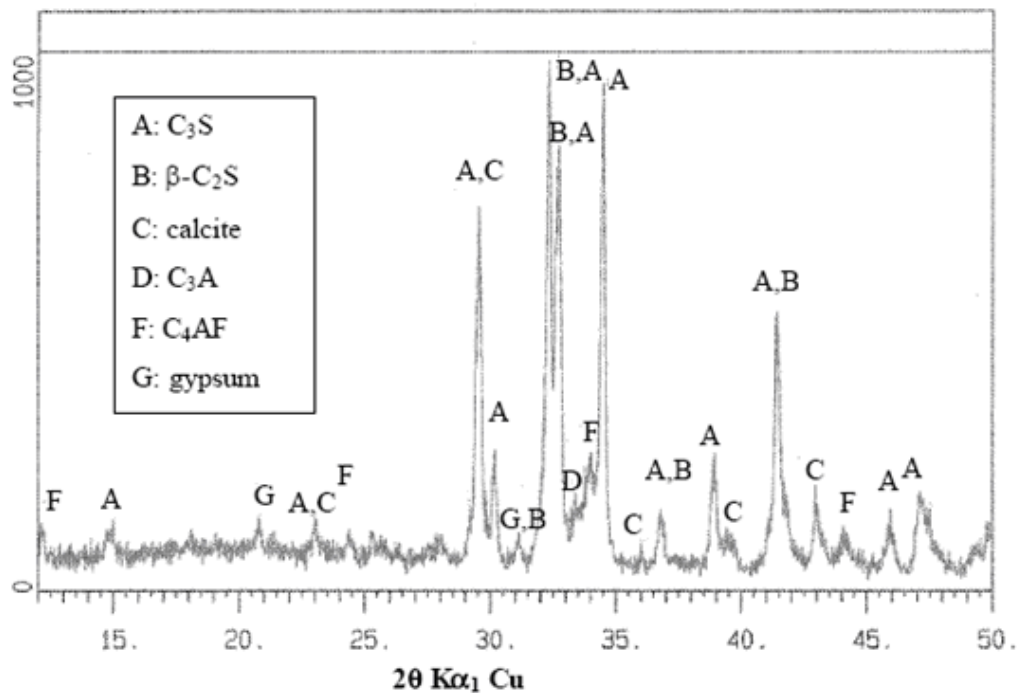


Fig 1 XR diffraction patterns of starting cement

Table (1) Chemical Composition of Materials (%)

Material	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O,Na ₂ O	SO ₃
PC	19.15	62.19	4.57	3.44	1.84	0.59	2.85

The apparatus and the experimental set-up for through-diffusion (leaching test)11

The whole apparatus in fig. 2 was constructed modularly and consists of transparent polystyrene allowing an easy check of the height of the solutions. The exterior measurements were about $(l \times w \times h) 20 \times 15 \times 12$ cm. The larger cavity was the reservoir for the source concentration, its total volume being about 600 ml. With the help of a membrane pump a smaller part of the reservoir side (volume $\approx 50 - 55$ ml) was continuously supplied with "fresh" solution from the larger part of the cavity. The pipes consist of PTFE, have a total length of about 1.0 m and an inner diameter of about 4 mm; the wetted parts of the pump are covered with PVDF, and the pump rate was about 15 - 20 ml/min, i.e. about 50 % of the maximum performance. The surplus of solution flows off an overflow back to the lower lying reservoir part of the cell. With such an arrangement a constant solution head was guaranteed. Due to the great amount of traced solution of the reservoir side the concentration on this side was kept nearly constant over a longer time span. Below the measurement cell there was a magnetic stirrer continuously mixing the solution in the measurement cell with the help of a small (Teflon covered) magnet. The temperature measured in the source solution changed in the interval of 25 - 35 °C 2, depending on the season. At the beginning of the experiments sorption of the tracer occurred at the walls of the diffusion cell and onto inner surfaces of pipes and pump. Therefore, daily and, later on, weekly checks of the reservoir concentration were performed by taking out 1 or 2 ml samples. Necessary corrections were made with the help of pre-calculated higher concentrated tracer solutions. The height of the liquid in the measurement cell had always to be at the same level as that of the reservoir side to avoid an additional driving force for diffusion due to a pressure gradient. The controlling and re-adjustment of this level after the sampling was done 'just by eye.

Table (2) Geometrical of the apparatus

quantity	symbol	unit	value
Volume of measurement cell	V	0.1^6m^3	52.0 ± 0.6
Volume of the tank side	V_0	0.1^6m^3	600 ± 35

When compared to the steady-state values for the diffusive flux, which was at least more than an order of magnitude larger it is evident that such additional fluxes can play a definite role only in the very early part of the tracer breakthrough curve. The volume of the measurement cell was determined to be 52.0 ml with an uncertainty of about 0.6 ml (0.6 % relative error). An ideal boundary condition at the low concentration side would have been an exact zero concentration condition which only was fulfilled at the very beginning of the experiments. For practical reasons in maximum a concentration of 1 % of that of the reservoir concentration side was accepted resulting in daily sampling, hence replacing of the whole liquid volume of the measurement side. However, in the (near) steady-state phase the concentration could periodically exceed this 1 % level of C_0 , yet only in the two days absence of the experimentalists during the weekends. After the weekends the maximum concentration in the measurement cell could be a few percent, but it was always well below 5 % of C_0 .

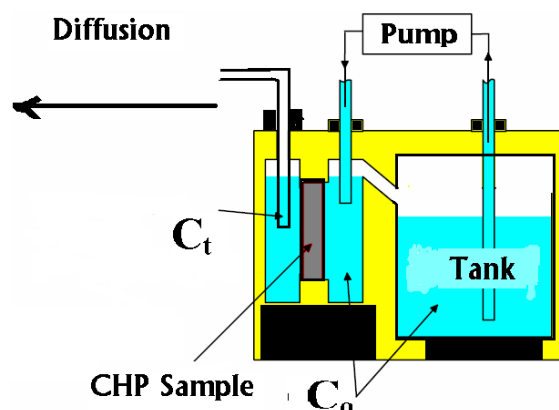


Fig 2 the sketch of the apparatus for the through – diffusion experiment “

HCP = hardent cement pastes;

C_0 = concentration of a given ion at the beginning of the first leaching interval;

C_t = concentration released from the specimen during the n th leaching interval.

Analysis of Leachants

All leachant analyses for ^{137}Cs were performed on a high purity germanium (HPGe) gamma spectroscopy system in accordance with specifications outlined in ANSI 42.14 - Calibration and Use of Germanium Spectrometers for the Measurement of Gamma-Ray Emission Rates of Radio-nuclides.[10] The 1.9 l polyethylene leachate containers also served as counting containers so no special sample preparation was required. Count times of 600 sec and 6000 sec gave minimum detectable activities (MDAs) for Cs of 1.38 Bq and 0.44 Bq, respectively. Use of longer count times to achieve lower MDA values was not warranted since the MDA value obtained at 6000 sec was considered negligible compared with the original activity spiked into each cement specimen, A_p . Counting times were of sufficient length to ensure counting errors were consistently below 20%. Leachant analyses provided the activity of the selenium released from the specimen during the n th leaching interval (a_n) [11] The leaching test was the a considerable amount of experimental data obtained from the samples, which maimed their dimensional integrity during leaching , indicate that internal bulk diffusion is the most likely rate – determining mechanism during the initial phases of the leaching process. Although additional mechanisms probably do occur to some degree, they are more likely to become rate determining only during later ages of leaching (19, 47 and 90). thus , the recommended data handling procedure of the standard is permissible , due to simplification of mass- transport theory (second Fick law at non- stationary stat) , for the purpose of clarifying and ranking solidified wastes , according to leachability . The solution of the mass- transport equations (second Fick law), for a specimen that be considered as a semi-infinity medium, permit the effective diffusion to be computed by:

$$D_e = \frac{V}{S^2} \left[\frac{C_n}{C_0} \right] / (\Delta t)_n \quad (1)$$

$$T = \frac{1}{2} (t_n^{1/2} + t_{n-1}^{1/2})^2 \quad (2)$$

Where

D_e is diffusivity factor

C_n is the activity or concentration released from the specimen during the n th leaching interval ;

C_0 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 seconds;

V is the volume of the specimen in cm^3 ;

S is the geometric surface area of the specimen in cm^2

interval for a semi-infinite medium .

Generally, this method to calculated " D_e " is valid up to 5 days of leaching time (abbreviated test) , where diffusion is the rate – detaining mechanism. At this point in the test , the T is the cumulative leaching time representing the " mean time " of the n th leaching specimen acts like a semi- infinite medium . from 5 days , the specimens , generally , acts like a finite medium, being the cumulative fraction leached higher than 20 % , and other methods to calculate " D " must be used . So, for example a graphical method or interpolation , from which the parameters "G" can be obtained , n this case

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

Where

d is the diameter of the specimen in cm , ,

G is the dimensionless factor As far as the leachability index "L" is concerned , it is a normalization factor , which is related to the specific material tested :

$$L = \log (\beta / D_e)$$

Where β is a defined constant ($1.0 \text{ cm}^2 / \text{s}$) . "L" also depends on the leaching condition and the leachant renewal schedule.

Leachability studies, therefore, consider all these variables and the results are applicable only to cases where all these the same within certain error range tables 4, present cumulative fraction release (CFR) values for each formulation at leaching intervals as specified in the ANSI/ ANS 16.1 -2003.

Results and discussion

1. Composition of the Aqueous Phase

Depending on the formulation of the cement-based binder system, different crystalline phases will be present at different curing durations. This would also vary based on the disposal environment. These crystalline phases would incorporate contaminants into their matrix, generally on a preferential basis. Leaching involves the attack of water on the calcium hydroxide and calcium silicate hydrate (CSH) present in hydrated cements. Solid hydrates of cement paste are more persistent at pH above 12-13, but at a lower pH the hydration phases no longer remain stable and thus dissolve. The pore solution of a typical portland cement paste is highly alkaline, so that the leaching process starts by removing alkalis (Na^+ and K^+), followed by dissolution of portlandite (CH) and subsequently by the leaching of calcium from silicates. Aluminate phases are also affected; depending on the formulation of the cement-based binder system, different crystalline phases will be present at different curing durations the aqueous phase and the concentrations of Ca and Si are shown in Table 2 and the relation between the leaching period and the composition of the aqueous phase is shown in Fig. 2. The results show that the pH and the concentration of Ca increase as the leaching period is extended, which indicates that the aqueous phase and the solid phase approach equilibrium with the development of dissolution.

The leaching period for which the values become constant was about 4 weeks for samples with a small liquid/solid ratio, and 5 weeks for ones with larger liquid/solid ratio. The cumulative amounts of Ca and Si dissolved in the aqueous phase after 16 weeks of leaching are shown in Table 3. As the liquid/solid ratio becomes larger, the amount of dissolved Ca increases and the Ca/Si molar ratio of the solid become smaller. The change in the solid phase composition could have affected the dissolution rate, which is considered as a cause of this trend. The concentration of Si in the aqueous phase also converged. However, the concentration of Si in samples with large a liquid/solid ratio increased at first and then decreased, finally converging at a specific value. It is considered that a large amount of Ca in the surface layer of the sample dissolved at the large liquid/solid ratio, which temporarily reduced the Ca/Si molar ratio in the surface layer. As C-S-H gel with a low Ca/Si molar ratio in the surface layer temporarily maintains equilibrium with the aqueous phase, the dissolution rate of Si was increased. The most important is a gel-like phase, designated C-S-H because it contains Ca, Si, and water (H_2O). This gel constitutes the principal binding phase. The gel phase is further restricted in composition because it largely excludes other chemical components of the paste from its crypto structure.

However, after the solid phase as a whole comes into equilibrium with the aqueous phase, the solid phase becomes homogeneous, leading to an increase in Ca/Si molar ratio and a decrease in concentration of Si. The pH and Ca concentration become constant in about 4 weeks for the samples with a small liquid/solid ratio and 8 weeks for the ones with larger liquid/solid ratio. The Si concentrations were constant after 13 weeks, which was considered to indicate that the solid phase entered into equilibrium with the aqueous phase after 13 weeks of leaching.

2- Relation between the Ca/Si Molar Ratio in the Solid Phase

The relation between the Ca/Si molar ratio in the solid phase and the composition of the aqueous phase after 13 weeks of leaching is given in Fig. 3. The Ca/Si molar ratio was calculated from the amount of Ca and Si dissolved in the aqueous phase. The pH and Ca concentration decreased when the Ca/Si molar ratio of the solid was small. The difference in the aqueous phase is considered to be due to this variation. However, the Ca/Si molar ratio in the solid phase after dissolution tests was obtained by calculation. Therefore, it will be necessary to analyze the chemical composition of the solid phase to compare it with the composition of aqueous phase.

Table 3 Chemical composition of leached water

Leaching Period weeks	Liquid/solid ratio (wt/wt)							
	30%		35%		45%		50%	
	Ca (mol/l)	Si (mol/l)	Ca (mol/l)	Si (mol/l)	Ca (mol/l)	Si (mol/l)	Ca (mol/l)	Si (mol/l)
1	1.54E-2	3.43E-5	1.22E-2	2.72E-5	3.53E-3	4.27E-5	3.75E-3	7.11E-5
4	2.11E-2	3.89E-5	1.00E-2	4.56E-5	4.44E-3	3.32E-5	3.87E-3	8.33E-5
8	1.04E-2	2.84E-5	1.99E-2	2.29E-5	5.25E-3	3.12E-5	5.12E-3	8.21E-5
12	2.07E-2	1.81E-5	2.09E-2	2.23E-5	6.51E-3	2.62E-5	6.64E-3	8.54E-5
16	1.87E-2	2.12E-5	2.00E-2	1.57E-5	7.23E-3	2.68E-5	7.56E-3	8.99E-5

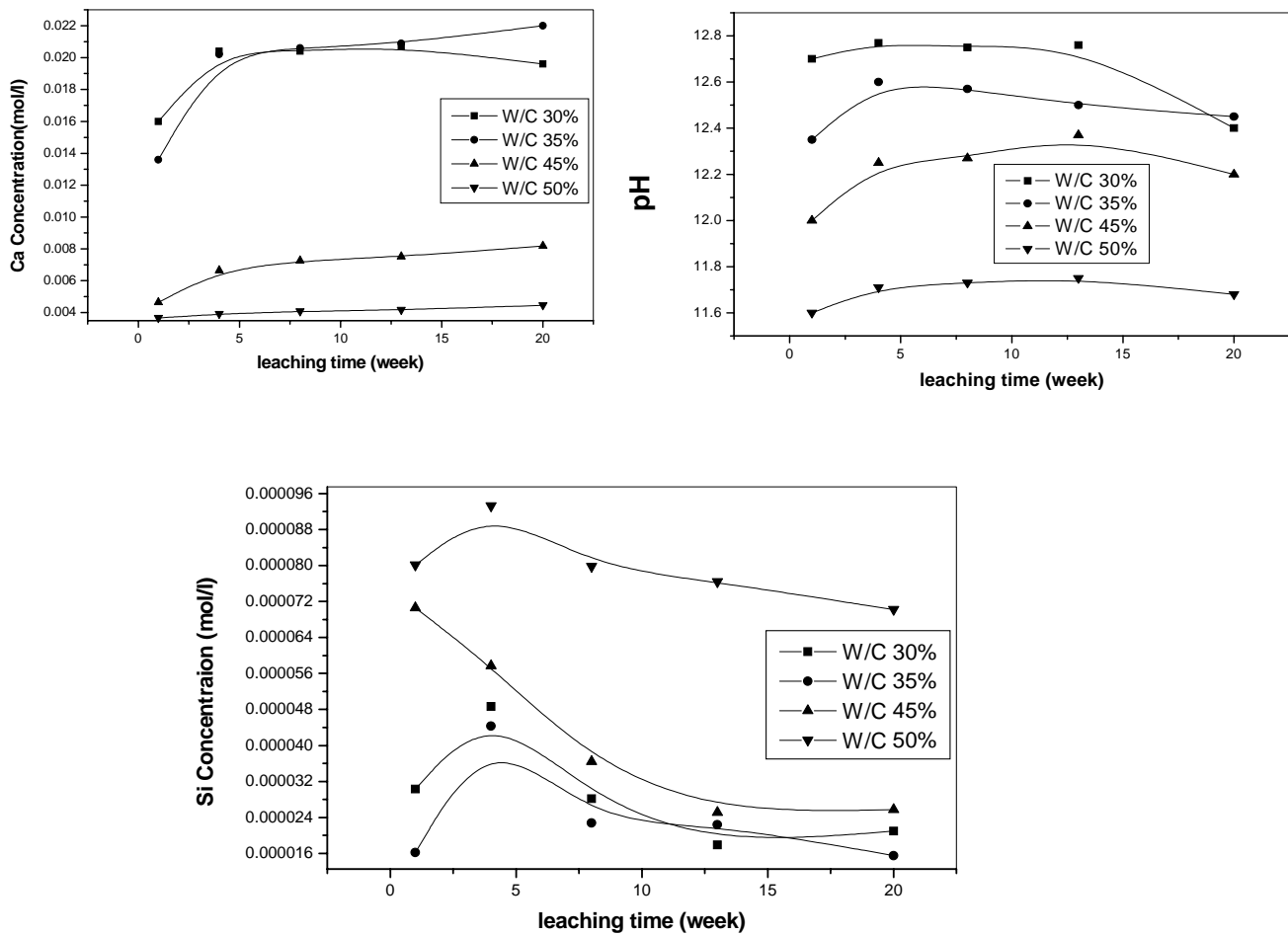


Fig. 3(A, B, C) Relation between the leaching pH period and the composition of the aqueous phase

Table 3 Cumulative amounts of Ca and Si dissolved in the aqueous phase after 12 weeks of leaching

W/C ratio	Ca/Si molar ratio of solid phase	Cumulative amount of element dissolved (mol)	
		Ca	Si
30%	3.04	2.07E-4	1.79E-7
35%	2.34	2.09E-3	2.24E-6
45%	1.98	3.43E-3	1.07E-5
50%	1.75	4.62E-3	2.32E-5
	1.01	5.00E-3	3.22E-4

3- Relation between Liquid/Solid Ratio and pH and Ca Concentration in the aqueous Phase

After 16 weeks of leaching is at equilibrium, the relation between liquid/solid ratio and pH and Ca concentration in the aqueous phase is shown in Fig. 4. The pH and Ca concentration are constant for liquid/solid ratios of 50% or less and decreases sharply for values of 30 lying between pH 10.5 and 12.5, is due to C-S-H dissolution. C-S-H dissolves incongruently from a C/S ratio, whereupon dissolution becomes congruent. The sudden drop in pH from pH 11.0 is due to exhaustion of the C-S-H phase. The most important is a gel-like phase, designated C-S-H because it contains Ca, Si, and water (H₂O). The gel compositions is confined to a rather restricted range of compositions ranging in Ca:Si molar ratios between about 1.7. This indicates that the dissolution mechanism of the solid phase to be dissolved had changed. A calculation using the amount of Ca(OH)₂ obtained by thermal analysis and the solubility of Ca(OH)₂ indicates that the Ca(OH)₂ will saturate for a liquid/solid ratio of 30% or less, the concentration of Ca decreases with the increase in the liquid/solid ratio. This interpretation illustrates well the results

shown in Fig. 4. Hence, the $\text{Ca}(\text{OH})_2$ in OPC hydrate under the test conditions in this study is considered to reach equilibrium after 16 weeks of leaching.

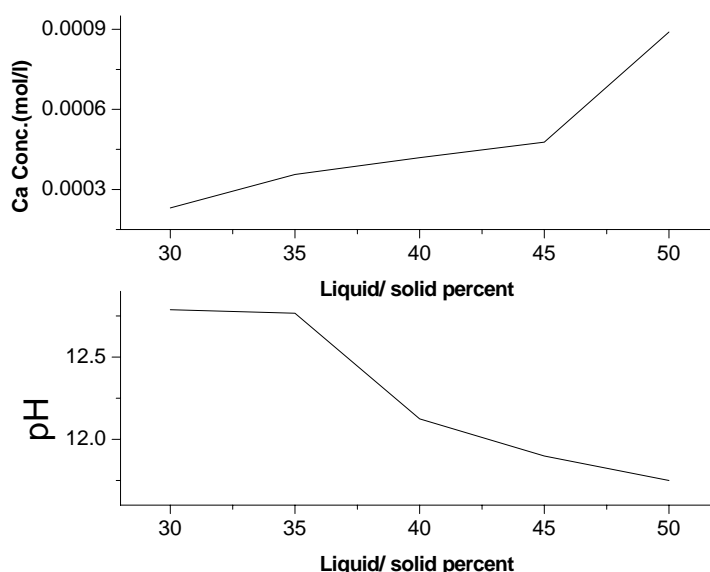


Fig 4 Relation between liquid/solid ratio and pH and Ca concentration in the aqueous phase

Phase Development in Blended Cements

For compares one from fig.1 and fig 5, the solid phases present. The most important is a gel-like phase, designated C-S-H because it contains Ca, Si, and water (H_2O). This gel constitutes the principal binding phase. The range of gel compositions is confined to a rather restricted range of compositions ranging in Ca:Si molar ratios between about 1. The gel is not totally without structure: it gives a very diffuse x-ray pattern which resembles an ill-crystallized version of the natural mineral tobermorite. Hence, this cement substance is sometimes referred to as 'tobermorite gel.' The analogy is not, however, satisfactory from the standpoint of either composition or structure: crystalline tobermorite has a composition which is fixed, or nearly so, at the Ca_5Si_6 ratio, and it has distinctly better crystallinity and lower solubility than C-S-H gel. Hence, a distinction should be made. The gel phase is further restricted in composition because it largely excludes other chemical components of the paste from its crystal structure. Alumina and some of the iron oxide in cement instead combine to form an aluminoferrite hydrate (hydrogarnet) and sulphoaluminate. The nature of the sulphoaluminate depends on the ratio of SO_4^{-2} to Al; high ratios favour ettringite, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31-32\text{H}_2\text{O}$, while low ratios favour "monosulphate," a calcium aluminate hydrate capable of allowing substitution of 2OH^- by SO_4^{-2} . In practice, the Fe content of these phases is very low, and may be neglected in their formula. The total quantities of Al, Fe, and SO_4^{-2} in a Portland cement are generally low, so the amounts of these phases which can develop is small, perhaps 10-15% of the total volume of the solid paste components. However, the chemical balance of OPC is such that not all Ca can be combined into these phases. For example, typical modern Portland cements have Ca:Si ratios ~ 2.5 , whereas the most Ca-rich C-S-H gel has a ratio of only ~ 1.7 . Therefore, much of the chemical excess of Ca appears as $\text{Ca}(\text{OH})_2$, portlandite. The three main phases of a well-hydrated Portland cement thus comprise an aqueous phase coexisting with two solids, $\text{Ca}(\text{OH})_2$ and C-S-H; the former is crystalline, while the latter is amorphous. The Aqueous Phase Even at low humidities, some capillary condensation of water occurs in cement pores and of course, many repository scenarios assume flooding, so an aqueous phase is always an important constituent of cement systems. Cement-equilibrated "water" has a high pH. It is in intimate contact with high surface area solids, a situation which favors equilibration and exchange. During the first few seconds of mixing, the mix water becomes strongly alkaline. It may also become supersaturated with respect to calcium during the first few minutes or hours of hydration; the solubility of $\text{Ca}(\text{OH})_2$ is about 1.67 g/L at 20°C, but if a cement powder is shaken with water for a few minutes, $\text{Ca}(\text{OH})_2$ solutions containing ~ 2.5 g/L are readily obtained. Such solutions are very labile; if filtered from cement and allowed to stand in a sealed container, they precipitate spontaneously. Much of the matter thus precipitated is colloidal or nearly so. If, however, Portland cement is allowed to hydrate at normal w/c ratios and the pore fluid is expressed after 28 d, super saturation will have been relieved and the pore fluid attained a steady state, or nearly so. Two factors combine

to lower drastically the Ca solubility in the pore fluid relative to its solubility in water. One factor is the discharge of super saturation, which lowers Ca solubility's towards the threshold set by $\text{Ca}(\text{OH})_2$ solubility. The other, more important, factor arises as a consequence of the alkali content of the cement ,(14,15).

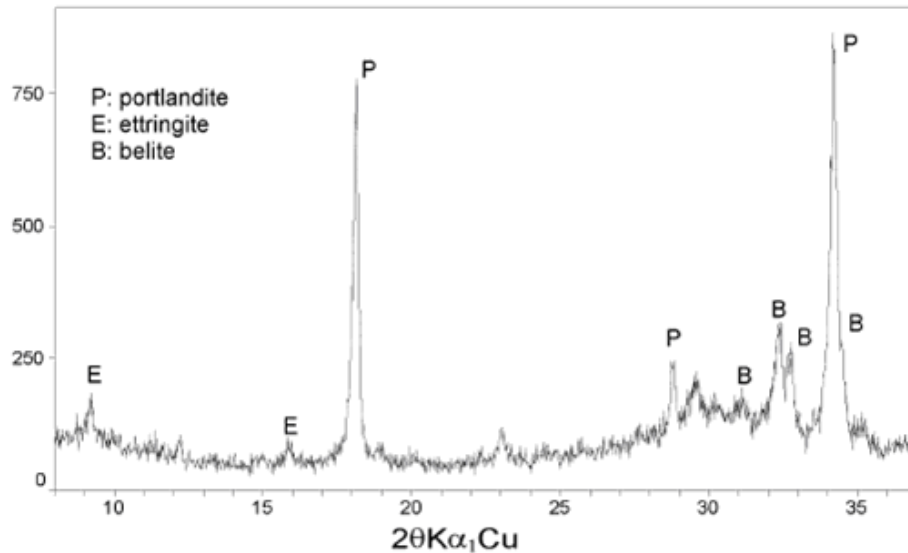


Fig 5 XRD Diffraction patterns of starting cement after 16 weeks

Analysis of leach ability waste

Among radioactive wastes arising during operation of nuclear power plants, the ^{137}Cs isotopes deserve attention from the point of view of immobilization due to its amount, half- life and high solubility. The conventional cementation technique is widespread for solidification of low and intermediate activity wastes [16] Cs mainly remains dissolved in the pore fluid of the cement matrix, from which it can readily migrate into the biosphere. Tables 5 and 6 present cumulative fraction release (CFR) values for each formulation at leaching intervals as specified in the ANSI/ANS 16.1 procedure. ANSI/ANS 16.1 defines cumulative fractional release as the sum of all fractions leached during all previous leaching intervals, plus the fraction leached during the last leaching interval ($\sum a_n / A_0$) using the initial amount of the species of interest present in the specimen as unity. All CFR values were corrected for radioactive decay back to the beginning of the first leaching interval. Uncertainties associated with each CFR value are experimental errors at the 1.0 sigma value for triplicate specimens. It clear he cumulative fraction release was increase when the W/C ratios increase .The diffusivity of the Cs through OPC at different times decrease due to caesium binding capacity of a cement matrix is significantly dependent on the chemical composition of the cement used, as the various phases formed during hydration have different binding capacity.

Table 5 Cumulative Fraction Release (CFR) values of Cs

Time (days)	30%	35%	45%	50%
0.083	3.02E-04	2.36 E-04	2.29E-03	7.45E-04
0.292	1.87E-04	2.2 7E-04	2.88E-03	1.87E-03
1	1.69E-03	2.55E-03	3.53E-03	3.39E-03
2	3.11E-03	3.26E-03	4.55E-03	4.56E-03
3	4.90E-03	5.79E-03	5.59E-03	7.35E-03
4	5.45E-03	5.9 5E-03	6.52E-03	8.69E-03
5	6.37E-03	56.37E-03	7.08E-03	1.03E-02
19	8.58E-03	7.48E-03	9.22E-03	8.58E-03
47	9.05E-03	9.95E-03	1.12E-02	1.23E-02
90	9.81E-03	1.06E-03	1.41E-02	1.33E-02

Table 6 diffusivity of the Cs through OPC at different times

Time (week)	Calculated diffusivity(m ₂ .hour ⁻¹)			
	30%	35%	45%	50%
1	1.32E-09	8.11E-09	2.22E-08	9.35E-08
4	9.36E-09	2.12E-08	6.82E-08	1.31E-07
8	2.01E-08	7.22E-08	1.1 1E-07	8.01E-07
13	1.11E-07	9.38E-07	2.43E-06	8.59E-06

Conclusions

In the repository environment, cements will undergo a variety of reactions. These reactions can be classified in two ways. Basically, either cement may be treated as a closed system with respect to transport of matter, or it may be treated as an open system; intermediate possibilities exist. Obviously the subject is extremely complex, and much of the information required in order to make predictions is site-specific in open system scenarios. Nevertheless, breaking the problem into its constituent parts provides a logical framework within which the problems can be solved. Cements are attractive matrices for the immobilization of radioactive wastes; they are inexpensive, tolerant of wet materials, durable in the natural environment, and draw upon existing technology.

The specifications for cement are quite strict, and imply definite limits to chemical and mineralogical compositions, and hence to their performance. Increasing the w/c ratio gives a more fluid mix (and also permits incorporating a higher proportion of liquid wastes) but the penalty to be paid is a rapid increase in the free, uncombined water content. This excess leads to a large increase in the total volume of larger pores (<0.1 μm), with corresponding increases in the permeability of the hardened product. If the role of cement is as a physical barrier, it must be formulated to a low w/c ratio; less rigorous restrictions may apply to grouts intended for space filling. Thus, in real situations, it may be necessary to compromise between fluidity, which implies higher w/c ratios, and impermeability, which implies the opposite.

The cement structures almost from the time of construction start to deteriorate in one form or another due to exposure to the environment (e.g., temperature, moisture, cyclic loadings, etc.). The rate of deterioration is dependent on the component's structural design, materials selection and quality of construction, curing, and aggressiveness of its environmental exposure

- The progress of degradation can be expressed in terms of water exchange cycles or speed of diffusion of ions in the pore solution. Cementitious materials are fundamentally unstable in water and change their properties with time.

1. Water is the single most important factor controlling the degradation processes of cement (i.e., the process of deterioration of cement with time is generally dependent on the transport of a fluid through concrete), little reduction in quantity of Ca⁺⁺ by lowering W/C ratio inductee that.
2. The aqueous phase reached equilibrium after 16 weeks from leaching.
3. The cumulative Fraction Released (CFR) of ¹³⁷Cs data suggest the reducing the W/C ratio of a cement formulation plays a somewhat limited role in its ability to immobilization of wastes and the immobilization may involve chemical fixation by formation of crystalline or noncrystalline compounds and sorption .
There are changes and some damage occurs in cement under the dynamic leaching test the XRD
4. The durability of cement based grouts under condition potentially found to be in nuclear waste repositories must studied

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