Long-term effect on the solidified degraded cellulose-based waste slurry in cement matrix

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The long-term effects on solidification/stabilization (s/s) of the secondary wastes, resulting from the oxidative degradation of some solid cellulosic-based wastes, in Portland Cement (CEM I) have been investigated by X-ray diffraction (X-RD) and Fourier transform infrared spectroscopy (FT-IR) techniques. The effect of seven years leaching of the cemented waste forms obtained was carried out to assess the long-term immobilization behavior of the radionuclide in the solidified/stabilized waste that maybe exposed to fresh, ground or sea water.

The results of this study confirm our previously published work that the oxidative degradation treatment of some cellulosic-based wastes is essential before incorporating into the cementitious inert matrix. In addition, the release of radionuclides from the cemented waste form is a diffusion controlling process, after the first washing out period lasting for nearly thirty days.

Based on the results so far obtained it is concluded that Portland Cement could be considered as a potential inert matrix to immobilize the degraded cellulosic-based wastes for a short or long time of storage or a final disposal.

Key words*: waste slurry, cement matrix*

Introduction

Organic solid cellulose-based waste (e.g. protective clothes, cotton, filter paper, towel paper, …) represent an important fraction of solid low and intermediate level radioactive wastes, originated from the peaceful applications of nuclear technologies in our life, and comprises in some cases up to 40 % of their composition (Pepper, 1981; Van Der Heyden and Debieve, 1995; Rahmann, 1995; Colasanti, et al, 1990). Therefore, many of these wastes have been identified as "problematic" because they are difficult to encapsulate using by conventional technologies and/or produce waste forms of poor quality (Saleh, 2004).

The wet oxidative degradation technique was chosen as a treatment process for oxidation and destruction of these waste categories, using 35 % hydrogen peroxide as oxidant, before the encapsulation process. The secondary waste slurry arising from this step was immobilized in Portland cement. The obtained solid waste forms were subjected to long-term aging (seven years). A chemical characterization of aged specimens was evaluated to obey the disposal environmental requirements.

The present study is a part of comprehensive research program carried out at the Radioisotope Department, Atomic Energy Authority aiming at the treatment and conditioning of low and intermediate level radioactive wastes.

Materials and methods

Degraded waste slurry

The degraded secondary slurry of some cellulose-based wastes was encapsulated in the cement matrix as a solidified waste form. The elemental composition and pH value of this waste slurry are given in tab. 1.

Tab. 1. Residual degraded slurry characteristics.

pH	Carbon [%]	Hydrogen [%]
1.5-2	1.0	4.3

Radioisotopes

The slurry waste solution was labeled with a mixture of Cs^{137} and Co^{60}, which best represent the famous radionuclides found in numerous types of low and intermediate level radioactive waste. These labeled specimens were used only for the chemical stability tests.

Cement materials

Portland cement CEM I 42,5N was a local cement manufactured according to the Egyptian Standard Specifications ES 4756-1/2005 and EN 197-1/2004 ES 2005). Table 2. represents the chemical analysis

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of the cement type and the composition of its four major compounds according to the Bogue calculation (Bogue, 1955).

Tab. 2. Chemical and compounds composition of the cement used.

Chemical composition [wt.%]		**Compounds composition** [%]	
SiO_2	19.84	**C_3S**	53.11
Al_2O_3	4.74		
Fe_2O_3	4.0	**C_2S**	16.89
CaO	61.01		
MgO	2.5	**C_3A**	5.81
K_2O	0.6		
SO_3	2.4	**C_4AF**	12.16
Insoluble residue	0.95		

Loss on ignition = 3.96 %.
Lime saturation factor = 96 % by wt.

Leaching solutions

Fresh, ground and sea water were used as leachants. The fresh water was obtained from the normal water in Giza district. Ground water was obtained from the Abu-Zaabel well (No.202) which is one of the nearest ground water wells to the Inshas-Reactor site. Sea water was obtained from Alexandria, on the Mediterranean Sea. The concentration of some interested ions of these three leachants is shown in tab. 3.

Tab. 3. Chemical analysis of some ions in different types of leachants.

Leachants	**pH**	**Soluble cations (ppm)**				**Soluble anions (ppm)**		
		K^+	**Na^+**	**Mg^{2+}**	**Ca^{2+}**	**Cl^-**	**SO_4^{2-}**	**HCO_3^-**
Fresh water	6.90	0.086	1.07	1.2	1.4	0.77	0.7	1.8
Ground water	7.20	23	149	13	74	137	317	272
Sea water	7.93	8.4	652.6	96.9	28.06	496.9	60.8	183

ppm ≡ mg/l

X-RD

X-RD analyses of the fresh and seven years aged solidified specimens were carried out by the Philips Analytical X-Ray B.V. apparatus operating with the Cu tube anode.

FT-IR

FT-IR analyses for cement waste forms identical to that subjected to X-RD were carried out by FT/IR - Jasco, 460 plus equipment Spectra usually recorded in the range of 4000–400 cm^{-1} with the 2cm^{-1} resolution.

*Leaching tes*t

The chemical stability of the solidified specimens containing the labeled secondary slurry having dimensions of 60±2 mm height and 31±0.5 mm diameters were evaluated by following the release of radionuclides from those specimens in different leachants. Leaching tests were performed according to the method recommended by the International Atomic Energy Agency (Hespe, 1971). The radionuclides content of the leachates were determined using the multichannel analyzer, PCAP, USA.

Results and discussion

It is not common practice to perform physical, mechanical or chemical testing of s/s products at a long time after the matrix has been prepared and disposed. Even though this study describes the changes that would have been detected after long-term testing (seven years) for Portland cement binding 35 % by weight slurry collected from the oxidative degradation of some solid cellulose-based waste.

X-RD analysis

The X-RD data of hydrated cement immobilizing 35 % secondary slurry after 28 days from casting and that aged for seven years are represented in tab. 4. and fig. 1. The results are in agreement with those reported by others workers (Taylor, 1990; Mollah et al, 2004; Helal, 2002). Upon mixing the slurry, which mainly composed of water, tab. 1., with the cement powder and molded for 28 days, they produced mainly portlandite {$Ca(OH)_2$},(CH), at d-values 4.88, 3.02 and 2.62 A^o with relative intensities of 100, 60 and 98.7 % respectively. Similarly, the peaks due to $CaCO_3$ (CC) are also in good agreement with those reported in literatures (d = 3.89, 2.48, 2.09 and 1.93 A^o with relative intensities 7.1, 4.6, 8.0 and 26.8 %) (Berry, 1974). The $CaCO_3$ phase appears as a result of secondary reactions of $Ca(OH)_2$ and C-S-H with atmospheric carbon dioxide. The micro crystalline C-S-H, generally as C-S-H-I and C-S-H-II, as the main hydration products, appears at the d-value of 8.7 A^o with the intensity 5.3 % and 2.55 A^o with the intensity 4.6 %, fig. 1. These values are highly comparable to those published by Helal (Helal, 2002). A careful investigation of aged specimen diffractogram indicates that the sample is composed mainly of portlandite {$Ca(OH)_2$}, carbonate-{$CaCO_3$} and C-S-H. It should be mentioned that the detection of portlandite in the aged specimen was rather unexpected it is supposed to be converted into $CaCO_3$ in the presence of atmospheric CO_2 over the long period of time (seven years). The same trend was reported by Helal (Helal 2002). This could be explained so because of the calcite formed through the reaction of $Ca(OH)_2$ and CO_2, during the progress of hydration by time, forming a protective layer coating the surface of hydrating particles and thus preventing a further reaction of $Ca(OH)_2$ with atmospheric CO_2. This could be confirmed through the decrease in the intensity of portlandite peaks at d-values of 3.02 and 2.62 A^o and the increase in the calcite peaks intensity at d-values 3.89 and 1.93 A^o, tab. 4. Other minor phases were developed which may be attributed to possible hydration products of PC, fig. 1.

Tab. 4. d-spacing (A^o) of main phases of hydrated Portland cement.

Phases	Fresh sample		Aged sample	
	d-spacing [A^o]	**Relative intensity** [%]	**d-spacing** [A^o]	**Relative intensity** [%]
Portlandite $Ca(OH)_2$	4.88	100	4.88	100
	3.02	60	3.02	53.4
	2.62	98.7	2.62	78.7
Calcite $CaCO_3$	3.89	7.1	3.89	10.5
	2.48	4.6	2.44	7.3
	2.09	8.0	2.09	10.1
	1.93	26.8	1.93	29.0

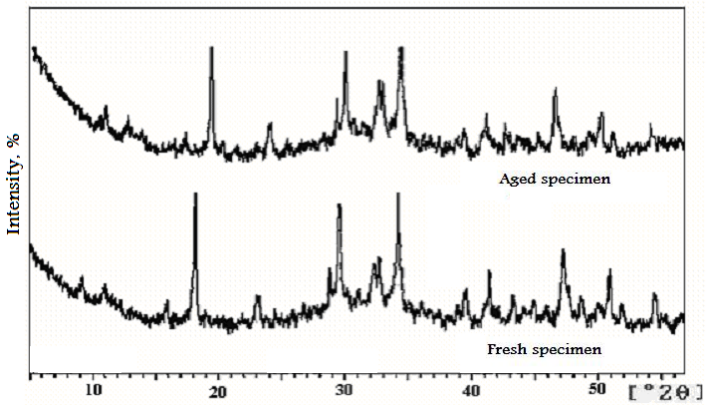

Fig. 1. X-RD diffractograms of the fresh solid cement specimens (28 days) containing 35 % of secondary slurry and that of the aged block (seven years).

FT-IR analysis

The FT-IR analysis for the solid cement blocks containing 35 % of secondary slurry solution was performed after 28 days of molding and after aging for seven years fig. 2. Peaks of the aged sample are in a good coincidence with that reported for the 28 days cured one. The IR-absorption spectrum of the hydrated cement waste forms is characterized by numbers of major absorption bands. The water region (symmetric and asymmetric vibrations or deformation vibration) describes a dynamic chemical system prevalent in a hydrating cement system. A broad band centered approximately at 3450 cm^{-1} is due to the symmetric and asymmetric stretching vibration of adsorbed water molecules while the same band in free water molecules in the vapor phase appears near 3650 cm^{-1} as a shoulder. This reduction in frequency is caused by the formation of moderately strong H-bonding. A second characteristic peak appears around 1640 cm^{-1} which may be assigned to the deformation vibration of water molecules in the set cement. The band near 1420 cm^{-1} may be referred to $Ca(OH)_2$ and $CaCO_3$ which were produced simultaneously during the setting and curing of cement in the presence of carbon dioxide. The hydration products of C-H-S can be identified basing on the sharp strong band around 1000 cm^{-1}. The peaks in the vicinity of 875cm^{-1} may be attributed to the stretching vibration mode of silicon dioxide (Si-O) in the hydrated cement, Fig. 2. This figure is in a good agreement with previous works reported (Kumerdarshan et al, 1990; Sugama and Kukacha, 1982; Herjndez et al, 1996). It is worth of mentioning that the bands assignment for the reference sample (cement mixed with water) and cured for 28 days show nearly the same values based on the data obtained by Saleh (Saleh, 2004).

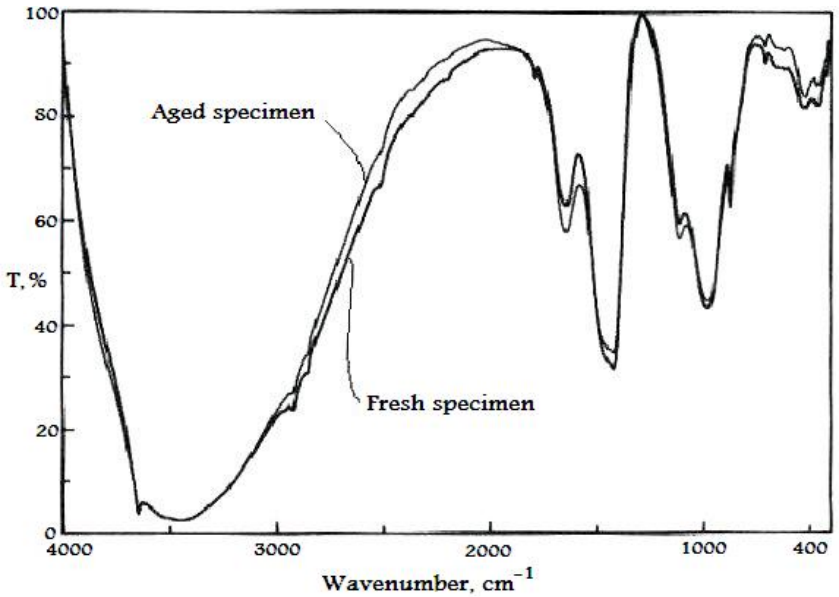

Fig. 2. FT-IR for the fresh solid cement specimens (28 days) containing 35 % of secondary slurry and that after seven years.

The data obtained from the X-RD and FT-IR analyses for seven years aged cement–waste form immobilizing 35 % of the secondary slurry originating from oxidative degradation of some cellulose-based solid wastes indicate that the cement is suitable as an inert matrix for the immobilization process.

Chemical stability

The responsibility of workers in the field of radioactive waste management is to provide the world with safe environmentally sound and publicly acceptable options for the long-term management of radwastes (Nirex, 2002). Near surface disposal facilities are designed to provide a long-term isolation for low and intermediate level radioactive wastes from the human environment by means of multi barriers systems. However, the solid waste forms can be the first and final barrier to release long-lived nuclides, a less attention have been paid to their long behavior in the disposal site (Ewing, 1995).

Leaching is generally considered as the basic criterion to evaluate the safety, acceptability and the chemical behavior of the final waste forms in the disposal site (Hwang and Teahwang, 1990). The cumulative leach rates of radionuclides were calculated for various cement blocks, containing the secondary slurry from the oxidative degradation process, after seven years period. The obtained rates are plotted against the square root of leaching time and the data obtained are represented in Figs (3-5). All the leaching curves are characterized by two distinct parts. The first one, where the activity of release increased in time up to nearly the first 30 days. This trend could be attributed to washing of the loosely

bounded surficial compounds of the cement blocks. Constant slopes of the second portion of the leaching curves would indicate that diffusion is the rate determining leach mechanism, for the seven years, according to Fick's first law (Sevensson and Allard, 2008).

It is clear from the data shown in fig. 3. that the cumulative leach fraction of radioactive components, from the cement waste forms containing different concentrations of labeled residual secondary slurry, in ground water after seven years are slight high at concentrations greater or lower than that at the value of 35 % slurry/cement (wt/wt). For the blocks containing less percentages (i.e. at 25 and 30 %), the high leach rates may be attributed to incomplete hydration of the cementitious materials that affects negatively the chemical behavior of the final waste forms. On the other hand, for cement blocks containing 40 % by of weight labeled residual secondary slurry, the excess solution remains unreacted. The volume occupied by that excess residual solution results in a formation of capillary pores in the set solid cement blocks and consequently increase its porosity. It should be born in mind that the same trend is recorded on three years leaching samples (Saleh, 2004) and the trend continued after then up to seven years of leaching for similar blocks and using the same leachant.

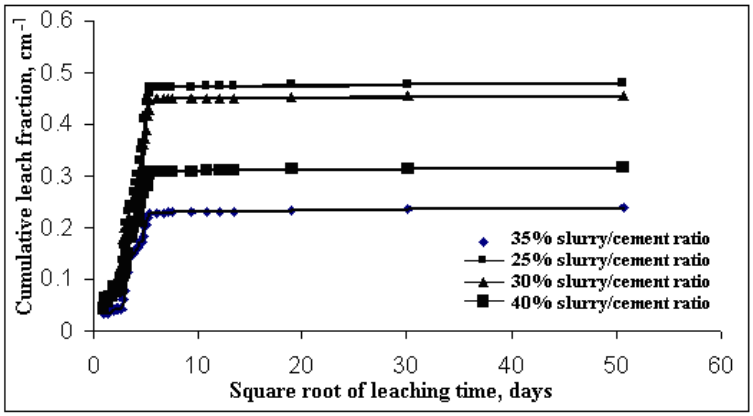

Fig. 3. Leaching behavior of cemented waste form containing different concentrations of degraded cellulosic waste slurry in ground water.

Fresh, ground and sea water represent the most obvious leachants that are supposed to get through the different proposed disposal sites for hazardous radwastes. The solid cement blocks containing 35 % of labeled slurry were subjected to leaching in these three different leachants for seven years period. It is clear from the data obtained in fig. 4. that the highest leach fraction was recorded for solid blocks submerged in fresh water while the ground water shows the lowest. This may be refered to the fact that calcium and magnesium ions present in sea and ground water, tab. 3., form insoluble hydroxide and carbonate in the alkaline medium of cement (pH = 13). These precipitates cause a partial sealing of cement blocks pores (Rubin et al, 1997) and consequently lowering the blocks porosity and decreasing the leachability of radionuclides from the final waste forms.

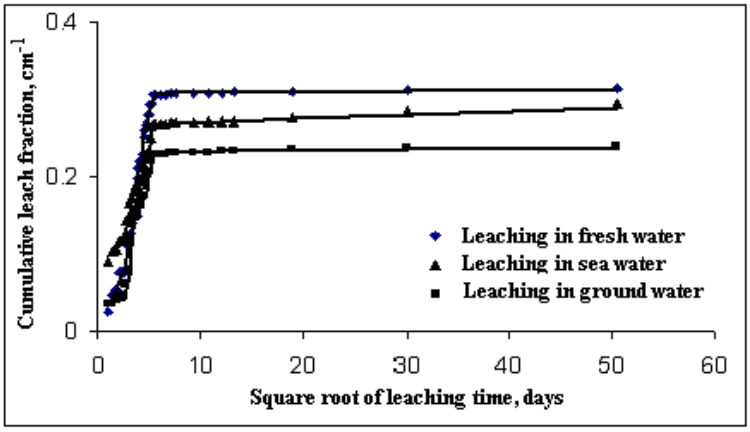

Fig. 4. Leaching behavior of cemented waste form containing 35 % of degraded cellulosic waste slurry in different types of water.

Freezing–thawing is one of the external adverse climatic conditions that may cause a physical disintegration of solid monoliths and consequently affects their apparent permeability, which leads to increase in the leachability of radionuclides hazardous components to the surrounding environment during a disposal period (Komarmeni, 1998). It is clear from fig. 5. that higher leach rates were obtained from the blocks subjected to the freezing-thawing treatment compared to the untreated blocks. In addition, increasing the freezing-thawing cycles was accompanied with a slight increase in the total cumulative leach fraction. The diverse in the leaching behavior of the PC blocks may be referred to the forest action. The hydraulic pressures generated by the increase of the pores volumes when the internal water freezes in cement cavities may cause undesirable effects on the leaching resistance of the final waste forms. However, it should be stated that after the first 30 days, the leachability of radioactive components from the hard monolith is nearly constant up to seven years of leaching period.

The leaching results presented in tab. 5. in terms of leachability index, a figure of merit inversely proportional to the logarithm of the effective diffusivity constant. The leachability index values greater than 6.5 were usually obtained representing acceptable values as compared to the minimum value of NRC leachability index criteria of 6.0. It is worth of mentioning that the leachability index can be employed to demonstrate that the waste form meets minimum quality assurance standards according to the guide line of Nuclear Regulatory Commission (NRC 1983).

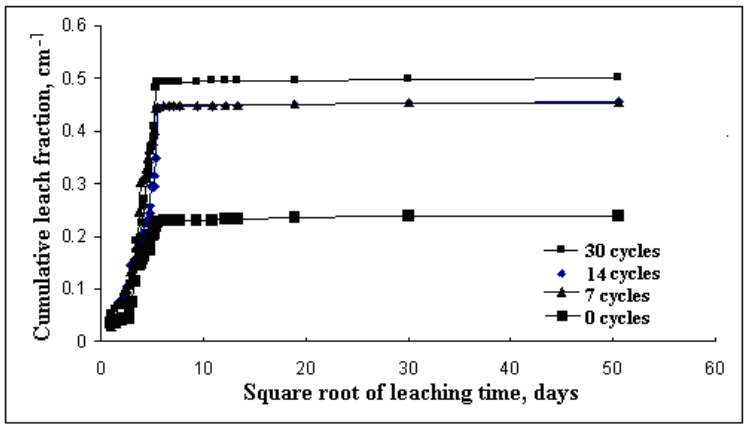

Fig. 5. Leaching behavior of the cemented waste form containing 35 % of degraded cellulosic waste slurry and subjected to different cycles of freezing-thaw condition.

Tab. 5. Effective diffusivity and average leachability index values of the PC form encapsulating degraded slurry of solid cellulose-based waste after seven years.

Type of waste form	**De** [cm^2/s]	**Lxi**
25%* leached in ground water	3.66742E-08	6.998679844
30%* leached in ground water	3.36968E-08	6.930714129
40%* leached in ground water	1.87665E-08	7.130110429
35%* leached in ground water	9.78605E-09	7.468530225
35%* leached in sea water	2.02844E-08	7.008740246
35%* leached in fresh water	1.7507E-08	7.197719517
35%* after 7 freezing-thaw cycles**	3.31129E-08	7.01580735
35%* after 14 freezing-thaw cycles**	3.04639E-08	7.098243404
35%* after 30 freezing-thaw cycles**	2.40577E-08	7.0627283

** Slurry/cement ratio*
*** Leached in ground water*

Conclusions

Encapsulation of contaminants within a waste form is the first of several barriers used to isolate radioactive hazardous from the accessible environment during the long-term disposal process it seems that. After seven years of leaching process in cement-waste forms immobilizing the secondary slurry from

the oxidative degradation of some solid cellulose-based wastes, the diffusion is controlling the leachability of radiocontaminants. In addition, the undetectable changes in the chemical and physical durability of the final solid waste form immersed for seven years in water, show the Portland cement as a favorite binding matrix for radwastes resulting in a durable waste form that can withstand anticipated conditions during storage, transportation and disposal conditions.

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