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Rice husk ash (RHA) as cement admixture for immobilization of liquid radioactive waste at different temperatures

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ABSTRACT

Cementitious materials will initially act as a mechanical barrier preventing activated water flow through the waste for a long time, and thus will contribute to the retardation of dissolved radionuclides by the combination of physical and chemical interactions. Most chemical species in aqueous solutions will undergo some kind of (chemical) interactions with any solids of the cementations material. Therefore, it is of great importance to develop a quantitative understanding of the chemical processes involved and to strictly differentiate between physical and chemical aspects of radionuclide transport through such materials. A study is undertaken to determine the waste immobilization performance of (Cs^+) wastes in cement–RHA mixtures. In addition to evaluating the effects of RHA on the leaching properties of cemented waste forms, the effect of addition of (RHA) on the strength of the cemented waste form is also investigated. However, RHA addition of 30% causes a significant increase in the hydraulic stability of cemented waste form. RHA enhances the strength; leaching and durability of cement may be through three primary actions which are the filler effect, the acceleration of ordinary Portland cement hydration and the pozzolanic reaction with calcium hydroxide (CH). The results were compared to control sample, and the viability of the RHA addition to concrete was verified. The use of these minerals results in ecological, economic and energy saving considerations.

1. Introduction

Solidification is one of the key technologies for removing hazardous wastes. The technique consists of entrapping the waste within a solid matrix having a high structural integrity, so that the risk of leaching from the waste body is reduced to minimum radioactive waste is an unavoidable by-product in nuclear energy production. After volume reduction and valuable component recovery, waste materials have to be conditioned by cement for transport, storage and disposal. Conditioning is the waste management step in which the radioactive waste is immobilized and packed. The objectives of immobilization are to convert the wastes into forms, which are (i) leach resistant and impermeable, so that the release of radionuclides will be slow even though flowing water may contact them and (ii) mechanically, physically and chemically stable for handling, transport and disposal. Cement is porous, continuously hydrating material whose actual surface area greatly exceeds its geometric surface area. In leaching, the rate of dissolution varies as a function of phase chemistry, and this dissolution exposes or enlarges pores; thus the leaching behavior must be related to the pore structure and to the composition of the pore solution. In order to avoid widespread dispersion of radionuclides into the human environment, radioactive waste produced in nuclear facilities has been incorporated in several kinds of matrices with different additives. The most important property of RHA that determines pozzolanic activity is the amorphous phase content. RHA is a highly reactive pozzolanic material suitable for use in lime-pozzolana mixes and for Portland cement replacement. RHA contains a high amount of silicon dioxide, and its reactivity related to lime depends on a combination of two factors: namely the non-crystalline silica content and its specific surface. Research on producing RHA that can be incorporated to concrete and mortars is not recent. In 1973, Plecas et al. [1] investigated the effect of preprocessing on the pozzolanic reactivity of RHA. The RHA used in this study was taken from Nagdy Island, Qalyub. The quantity was taken in plastic bags, transported to the laboratory and then stored for subsequent uses; the objective of this research is to provide information on the utilization of RHA as a supplementary cementing material for producing high-performance concrete and reduced wastes diffusivity through the matrix under the temperature of 25, 60 and 150 °C compared with control sample [1–6].

2. Materials and mortar composition

2.1. Materials and method

2.1.1. Cement
RHA and ASTM Type I normal Portland cement was used. The physical properties and chemical properties of the cement are

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Table 1
Physical properties and chemical analysis of cement and RHA

	ASTM Type I cement	RHA
Physical test		
Specific gravity	3.09	2.06
Passing 45 μm, present	93	99
Specific surface, Blain, m^2/kg	373	–
Nitrogen adsorption, m^2/g		38.9
Setting time, min:		
Initial	135	
Final	222	
Chemical analyses, percent		
Silicon dioxide (SiO_2)	20.1	87.2
Aluminum oxide (AL_2O_3)	4.51	0.15
Ferric oxide (Fe_2O_3)	2.5	0.16
Calcium oxide (CaO)	61.3	0.55
Magnesium oxide (MgO)	3.13	0.35
Sodium oxide (Na_2O)	2.24	1.12
Potassium oxide (K_2O)	0.39	3.68
Phosphorus oxide (P_2O_3)	<0.9	0.5
Titanium oxide (TiO_2)	0.24	0.01
Sulfur trioxde (SO_3)	4.04	0.24
Carbon (C)	–	5.91
Loss on ignition	2.41	8.55
Bogue potential compounds		
Tricacium silicate (C_3S)	51.3	
Dicalcium silicate (C_2S)	19	
Tricalcium aluminate (C_3A)	7.7	
Tetracalcium aluminoferrite (C_4AF)	7.6	

given in Table 1. The cement was used in this study from Tora Com., Egypt.

2.1.2. Rice husk ash (RHA)

RHA used was a processed waste material incinerated at a temperature not exceeding 800 °C for a few minutes. The chemical composition and physical properties of the RHA are also are summarized in Table 1. The RHA contains a carbon content of 5.91%, and therefore it is black in color. Chemical analysis indicates that the material is principally composed of SiO_2 (87.2%), and is also high in loss on ignition (8.55%). The ash also contains a relatively high K_2O content of 3.68% that originates mainly from the soil or due to the use of fertilizer [7]. RHA has a specific gravity of 2.06. Particle size distribution of the material is shown in Table 1, together with that of the Portland cement used in this study. Particle size distribution was determined by a particle size analyzer using scattered light from laser beam projected through a stream of particles suspended in isopropanol. The amount and direction of the light scattered by particles were then measured by an optical detector and analyzed by a computer. The medium particles size of the RHA is approximately 7 μm, while that of the cement is approximately 13 μm. The RHA, however, has an extremely high specific surface of 38.9 m^2/g by nitrogen absorption, which is almost 1.5 times for silica fume. The RHA used in this experimental program was obtained by incineration of RHA in a control oven at a burning temperature not exceeding 800 °C for few minutes. X-ray diffraction of cement and RHA are shown in Figs. 1 and 2. The X-ray diffraction analysis indicates that the ash contains mainly amorphous materials with a small quantity of crystalline phases as silicate (high-temperature phase of SiO_2) and KCI. The amorphous silica present in the RHA is responsible for the pozzolanic activity of the ash. The RHA has an extremely high specific surface of 38.9 m^2/g by nitrogen absorption. According to Plecas et al. [1], the carbon is intimately distributed in the amorphous silicate structure, and the high specific surface of the RHA is due to its honeycomb microstructure, not due to its high carbon content.

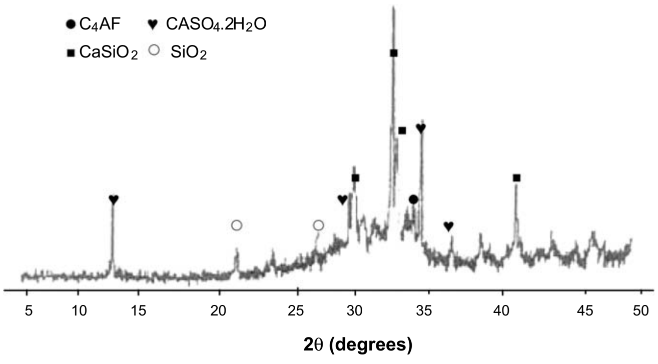

Fig. 1. X-ray diffraction of ASTM Type I cement.

2.1.3. Fineness and the average particle size

The grinding time was changed gradually from minutes to 2 h to study the effect of this change on the specific surface area and the particle size. The specific surface area is determined by using Blaine fineness test. Micro-track method is used to measure the particle size in order to establish the relationship between fineness and particle size of rice husk ash with the grinding time, which is indicated in Fig. 3. From the results of the fineness and the grinding time, it is concluded that the prolongation of grinding time more than 60 min does not necessarily results in the increase of the specific surface area by any noticeable value, whereas the increase from 5 to 10 min is very large, giving straight lines, which is reflected in the results of the particle size.

The relationship between fineness, grinding time, and particle size of RHA [8–9] is:

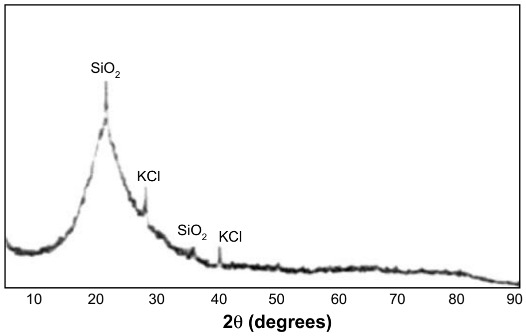

Fig. 2. X-ray diffraction of RHA.

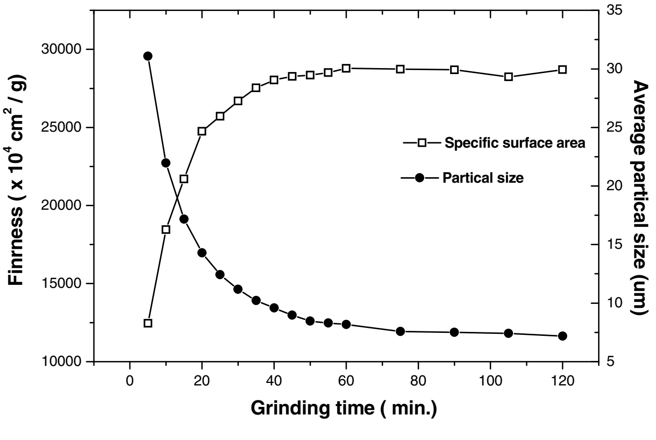

Fig. 3. Particle size and fineness of RHA vs grinding.

$$D = a + bF = cG_1$$

where F is the fineness (cm^2/gm), G_1 is the grinding time (min), and *D is the* particle size (µm).

2.1.4. Mix proportions

Different mixes of ordinary Portland cement (OPC) mortar of different *W*/(OPC + RHA) ratios were prepared. Different percentages of RHA (0%, 10%, 20%, 30%, 40%, and 50%) were considered in the matrix as a cement replacement material. These specimens were cast in 7 × 7 × 7 cm cubes and then water cured for different curing periods (28, 90 and 270) and these cubes were tested for compressive strength immediately after their consecutive curing periods.

3. Results and discussion

3.1. Physical properties

The Vicat needles were used to determine the rate at which cement pastes harden paste specimens that were prepared under standard condition and cured at constant temperature and humidity. Initial and final setting time tests were performed on plain cement paste and pastes having rice husk ash. RHA is used to study the effect of particle size or surface area increase on the setting time of pastes. The content of RHA is 10%, 20%, 30%, and 40% by weight of cement, respectively. Just like other hydraulic cement, the reactivity of rice husk ash cement depends very much upon the specific surface area or particle size. The rice husk ash cement with a finer particle exhibits superior setting behavior and hence higher compressive strength. Fig. 4 shows the results of water/cement ratio for the standard consistency of cement paste with RHA.

Fig. 5 shows the results of setting times of different pastes. The results show that increases in initial and final setting times for cement–RHA pastes over those of plain cement paste. The results also show that the setting times increased with the increasing content of RHA in pastes. This may due to the slower pace of heat induced evaporation of water from the cement–RHA.

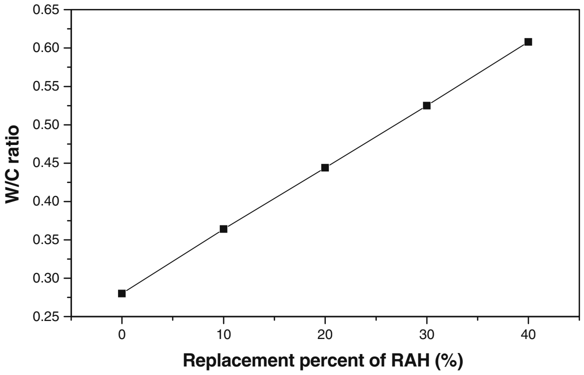

Fig. 4. Water/cement ratio for standard consistency of cement paste with RHA.

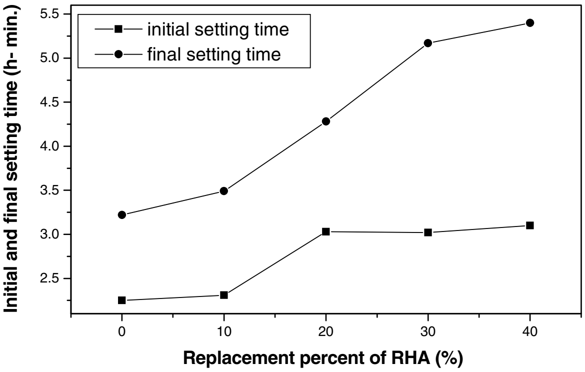

Fig. 5. Initial and final setting times of RHA with different replacement percentages.

3.2. Pozzolanic activity of ash

The chemistry of rice husk ash cement involves the chemical reactions of the amorphous silica in the ash with lime to form calcium silicate hydrates. The compounds in cement primarily are responsible for the strength. In the case of a mixture of Portland cement–rice husk ash, the silica reacts with extra lime in the Portland cement, which in some cases can be as high as 60%. The silicates formed are of the kinds: CSHI and CSHII; the reaction may be illustrated [10] as:

$$\text{Ca(OH)}_2 + \text{SiO}_2 = \text{CSHI} + \text{CSHII}$$

where

$$\text{CSHI} = \text{CaO}_{1.5-2.0}\ \text{SiO}_2(\text{H}_2\text{O})_{1.0-2.5}$$

$$\text{CSHII} = \text{CaO}_{0.8-1.5}\text{SiO}_2 2(\text{H}_2\text{O})$$

The type of the ash suitable for the pozzolanic activity is amorphous rather than crystalline ash. It has been established that the silica in the ash undergoes structural transformations under varied temperature conditions. Incineration of rice husk in the temperature range of 550–700 °C is generally found to produce amorphous silica in the ash, while temperature in excess of 900 °C produces unwanted crystalline forms. Fig. 6 shows the effect of RHA content on the total porosity of RHA-hardened cement paste. When the percent of the RHA was increased, the total porosity decreased. This decrease in the total porosity is attributed to the change occurring in the pore size distribution as a result of using RHA which could react with the calcium hydroxide to form CSH.

3.3. Crystal structure of RHA paste

X-ray diffraction analysis was performed at the age days for the three cases of hydrated cement pastes OPC/RHA (0%, 20% and 30%) shown in Fig. 7. The diffractograms demonstrate that the height of peaks characterizing the portlandite phase [Ca(OH)_2] decreased with increasing of the RHA content. The calcium hydroxide released during cement hydration was consumed as a result of interaction with active amorphous silica present in the RHA to form the CSH phases, which could contribute to the increase in the compressive strength. On the other hand, the peak of CaCO_3 increased as a result of increasing RHA content. The results of X-ray diffraction for 30% interpret the increase the compressive strength for the same case of 0.4 *W*/(OPC + RHA), where calcium hydroxide during

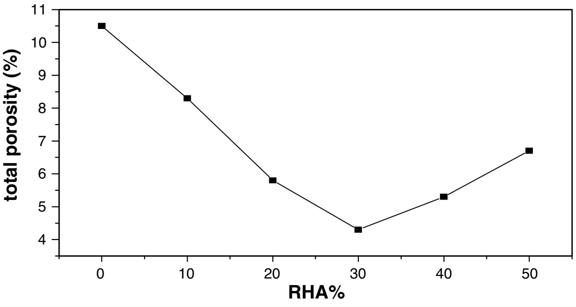

Fig. 6. Total porosity of RHA hardened cement paste.

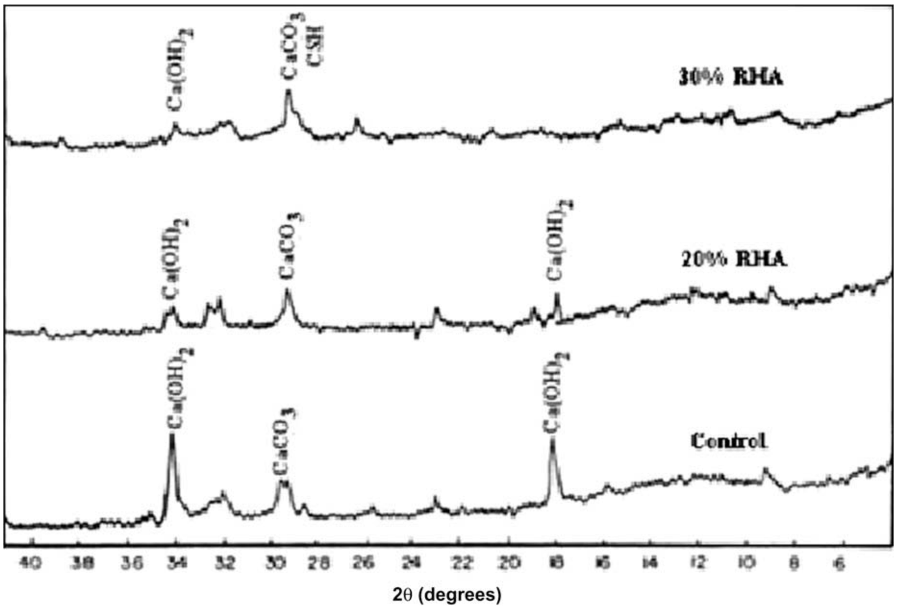

Fig. 7. X-ray diffraction of cement pastes with 0%, 20% and 30% RHA.

hydration is actually consumed during its reaction with amorphous silica present in the RHA to form the CSH phases.

3.4. Phase composition of RHA-hardened cement paste

Fig. 8 indicates the DTA of the layer for the hydrated cement paste containing RHA (0.20% and 30%). The thermograms illustrate the existence of endothermic peak located at 100 °C, due to the decomposition of CSH. The second endothermic peak was observed at about 470 °C, representing the decomposition of calcium hydroxide [$Ca(OH)_2$]. The third endothermic peak was located at about 740 °C, representing the thermal decomposition of calcium carbonate ($CaCO_3$). The peak of CSH increases for 30%, which agree with our compressive strength results where CSH increase contributes to the strength.

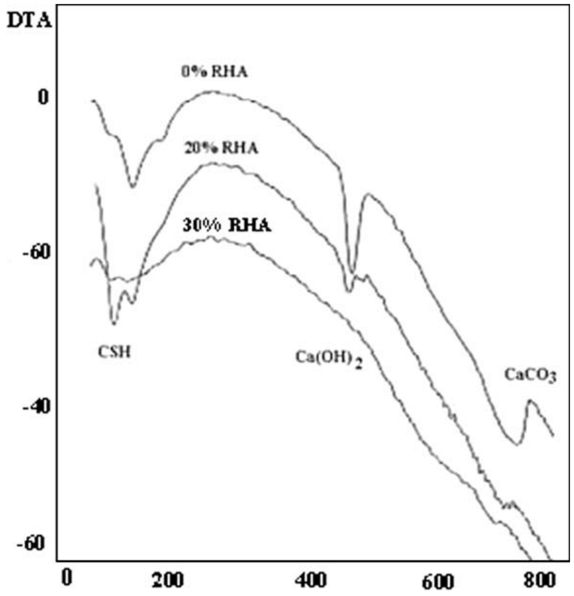

Fig. 8. DTA curves of the fifth layer (bulk) for the cement pastes containing 0%, 20% and 30% RHA.

4. Mechanical properties

Compressive strength tests were carried out on the RHA–cement mortar cubes of different *W*/*C* ratios (0.4, 0.5 and 0.6) which were tested at the end of three curing periods (28, 90 and 270). Each reported result of the compressive strength was considered as an average of three specimens. Figs. 9–11 show the effect of RAH content on the compressive strength for different curing periods and different *W*/*C* ratios. The compressive strength increases as time of curing increases, but the rate of strength development is high in the early age. Using of RAH (10%, 20% and 30%) as a replacement of cement led to an increase in the compressive strength for all periods of curing. From all test results obtained, it was found that using of 30% RHA as a replacement of part of cement could be considered optimum for all content of *W*/*C* ratios investigated mortars because of its high values of compressive strength. Fig. 12 shows the effect of *W*/*C* on the compressive strength for 30% RHA cured with water for 28, 90 and 270 days. It is clear that for all periods of curing time, the compressive strength decreased with the increase of *W*/*C* ratios. Cement normally consists of voids and also micro cracks. In the early stage of mixing, the calcium silicate hydrate (C–S–H) phase in hydrated Portland cement is compact but contains capillary cavities or voids, which exist when

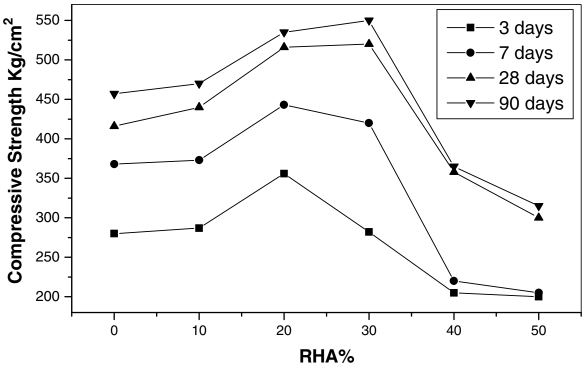

Fig. 9. The effect of the RHA content on the compressive strength for mortar cubes at different curing periods (*W*/(OPC + RHA) = 0.4).

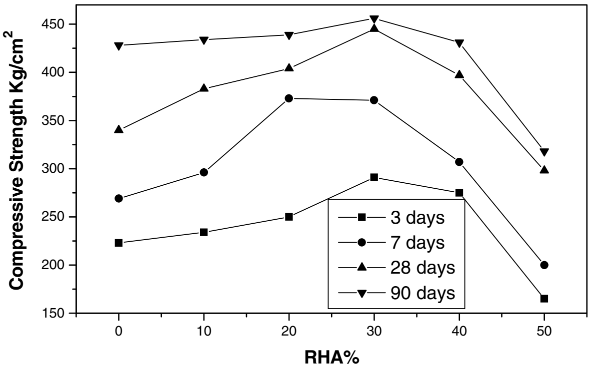

Fig. 10. The effect of the RHA content on the compressive strength for mortar cubes at different curing periods (W/(OPC + RHA) = 0.5).

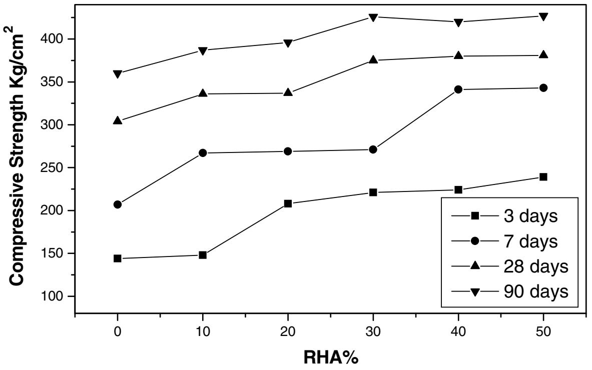

Fig. 11. The effect of the RHA content on the compressive strength for mortar cubes at different curing periods (W/(OPC + RHA) = 0.6).

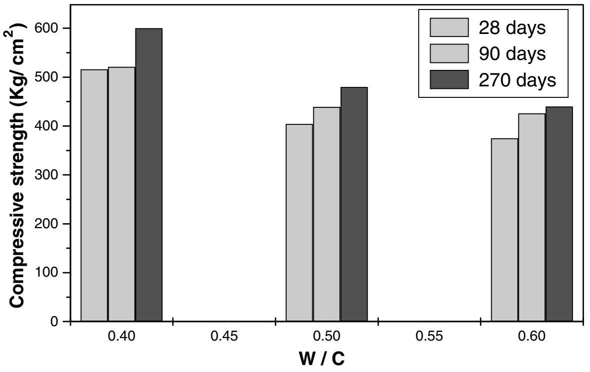

Fig. 12. The effect of the RHA content on the compressive strength for mortar cubes at different curing periods (W/(OPC + RHA) = 0.6).

the spaces originally occupied with water do not get completely filled with the hydration products of cement. The mineral mixtures are very fine particles that reduce the voids and fill the micro cracks in concrete. The pozzolanic reaction converts the compact C–SH phase with large cavities to low-density C–S–H products with smaller voids.

5. Leaching procedure

The leach characteristics, which refer to the release of radionuclides from the solidified waste-forms to aqueous environment at different temperatures (25–150 °C), were reported by using RHA to Portland cement. I was used as a bath-containing oil to increase the temperature to 150 °C. Radioactive wastes containing Cs-137 was incorporated into matrices. Leaching experiments were carried out following Hesp's leaching test [11]. In all leaching experiments, the samples were suspended in a way that the whole surface area was exposed to the leaching solution. Cs-137 activity was measured using a gamma-spectrometer with 4 \ \ × 4 \ \ NaI crystal activated with thallium. The crystal is connected to a multichannel analyzer with software package. The results shall be expressed by Figs. 13, and 14 of the cumulative fraction of radioactivity leached from the specimen as a function of the total time of leaching. The specimens were cast in 2 × 2 × 2 cm cubes that were tested for leaching for different curing periods; the matrix consists of 70% cement, 30% RHA at W/(OPC + RHA) ratio = 0.4 at different temperatures.

$$\left(\sum a_{\mathrm{n}}/A_{\mathrm{o}}\right)\Big/(S/V) \text{ versus } \sum \sqrt{t_{\mathrm{n}}}$$

or

$$\left(\sum a_{\mathrm{n}}\Big/A_{\mathrm{o}}\right) \text{ versus } \sum \sqrt{t}$$

where a_{n} is the radioactivity leached during the leachant renewal period n; A_0 is the radioactivity initially present in the specimen; S is the exposed surface area of the specimen (cm^2); V is the volume of the specimen (cm^3); t_{n} is the duration (days) of leachant renewal period.

leach coefficient, D, is used, and it is defined as

$$D = \pi/4\ \mathrm{m}^2\mathrm{V}^2/\mathrm{S}^2$$

where D is the leach coefficient (diffusion) (cm^2/d) or (cm^2/s); m is the $(\Sigma A_{\mathrm{n}}/A_0)\cdot(1/\sqrt{\Sigma t})$, slope of the straight line (d$^{-1/2}$); A_0 is the initial sample activity at time zero (Bq); (Table 1) A_{n} is the activity leached out of sample after leaching time t, (Bq); t is the duration of leaching renewal period (d); (1,2,3,4,5,6,7,15,30,60) V is the sample volume (cm^3); S is the sample surface (cm^2).

The cumulative fractional release (CFR) data show a decrease in Cs leachability of a cement formulation concomitant with rice husk ash (RHA). This effect is illustrated in Figs. 13–17. Table 3 shows the Cs diffusivity through OPC and OPC + 30% RHA at different temperatures. I was used as a bath-containing oil to increase the temperature to 150 °C. The addition of RHA tends to result in mixes that are better able to immobilize the Cs. Since RHA is known to have sorption capacity for anions, the reduction in leachability may be due to the physical effects, i.e., blocking of cement pores with fine particles of (RHA) and may be due to the chemical effect through the modification of the cement microstructure through

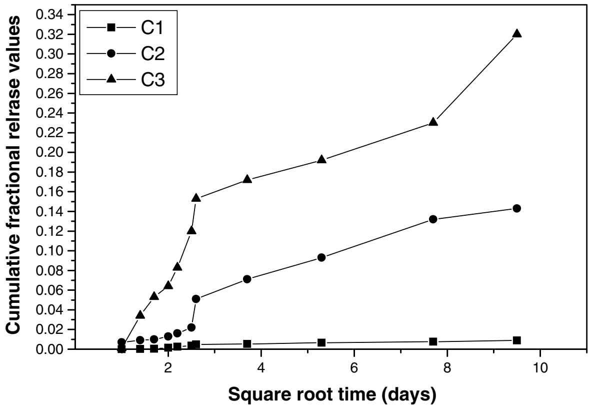

Fig. 13. Damaging effect of temperature on the leachability of 137-Cs for 100% OPC and W/(OPC + RHA) = 0.4.

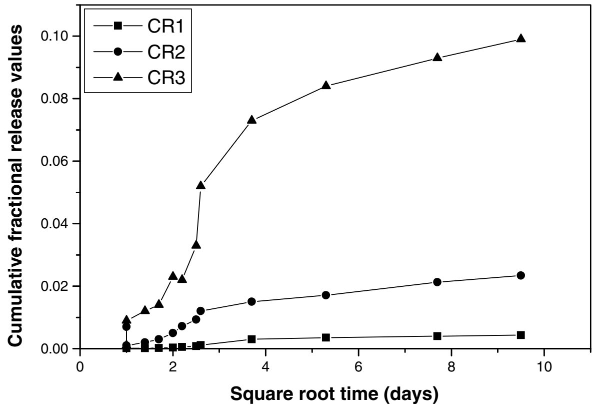

Fig. 14. Damaging effect of temperature on the leachability of 137-Cs for 70% OPC + 30% RHA and *W*/(OPC + RHA) = 0.4.

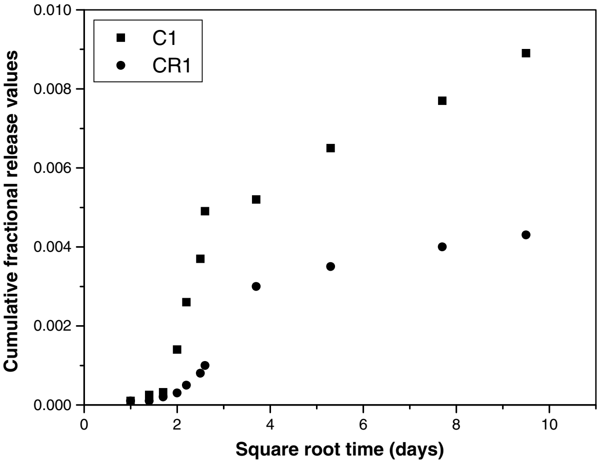

Fig. 15. Comparison between the effect of temperature on the leachability of 137-Cs for 70% OPC + 30% RHA cured at 25°C.

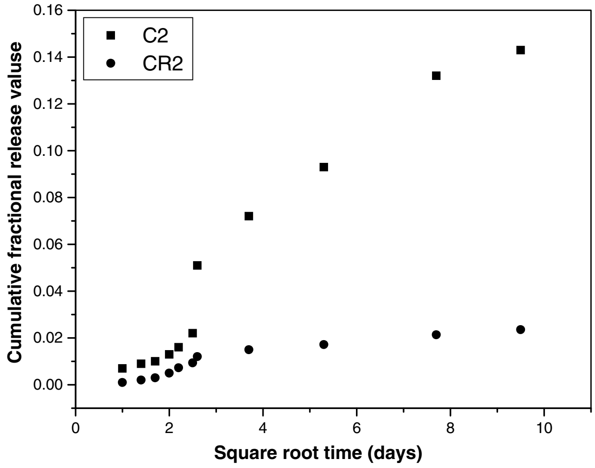

Fig. 16. Comprasion between the effect of temperature on the leachability of 137-Cs for 70% OPC + 30% RHA cured at 60°C.

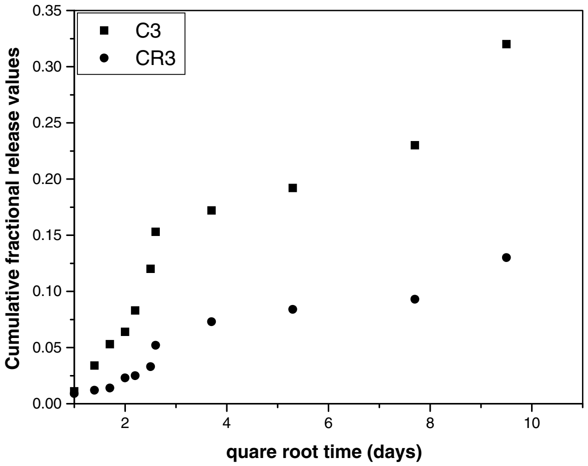

Fig. 17. Comparison between the effect of temperature on the leachability of 137-Cs for 70% OPC + 30% RHA cured at 150°C.

Table 2
Cement mixtures proportions at 30% RHA and *W*/(OPC) = 0.4

Sample No.	% Cement (OPC)	% RHA	Cured temperature (°C)
C1	100%	0	25
C2	100%	0	60
C3	100%	0	150
CR1	70%	30%	25
CR2	70%	30%	60
CR3	70%	30%	150

Table 3
Cs diffusivity through OPC and OPC + 30% RHA at different temperatures

Sample	Calculated diffusivity (m^2/s)	Cure temperature (°C)
C1	3.6×10^{-13}	25
C2	1.5×10^{-11}	60
C3	5.6×10^{-11}	150
CR1	6.4×10^{-13}	25
CR2	1.7×10^{-11}	60
CR3	8.1×10^{-11}	150

the production of additional tricalcium silicate, especially C_S. Binding capacity of a cement matrix is significantly dependent on the chemical composition of cement and additive used, as the various phases formed during hydration have different binding capacities [12,13] (see Table 2).

6. Conclusions

- RHA is a highly reactive pozzolanic material and can be used as a supplementary cementing material to produce high – performance concrete and to produce a highly effective supplementary cementing material and reduce the environmental impact of uncontrolled burning of rice by products.
- The compressive strength of the concrete containing up to 30% of the RHA was higher than that of the control Portland cement. The strength of the concrete increased with decreasing *W*/*C*.
- RHA can react with Ca $(OH)_2$ released by cement clinker hydration to produce secondary C–S–H gel inside the cement paste, the secondary formed C–S–H gel improved the microscopic property of cement.
- Data indicated that formulation with low *W*/*C* and increased level of RHA up to 30% resulted in formulations that improve the retention of radionuclides such as C_S. Cesium binding capacity of a cement matrix is significantly dependent on

the chemical composition of cement and additive used, as the various phases formed during hydration have different binding capacities.

- The use of these minerals results in ecological, economic and energy saving considerations.

In the production of high strength, low permeability concrete, for use in bridges, marine, environments, and nuclear power plants, RHA has been added to the Portland cement. It boosts the chemical reaction called the 'pozzolanic' reaction, where hydration (mixing with water) of Portland cement produces many compounds, including calcium silicate hydrates (CSH) and calcium hydroxide (CH). The CSH gel is known to be the source of strength in cement. When RHA is added to fresh cement, it chemically reacts with the CH to produce additional CSH. The benefit of this addition is twofold: increases compressive strength and decrease leachability.

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