Durability of Gamma Irradiated Polymer Impregnated Blended Cement Pastes

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ABSTRACT
This study is focusing on durability and performance of the neat blended cement paste as well as those of the polymer-impregnated paste towards seawater and various concentrations of magnesium sulfate solutions up to 6 months of curing. The neat blended cement paste is prepared by a partial substitution of ordinary Portland cement with 5% of active rice husk ash (RHA). These samples were cured under tap water for 7 days. Similar samples were impregnated with unsaturated polyester resin (UPE) and subjected to various doses of gamma rays ranging from 10 to 50 kGy. The results showed that the irradiated impregnated specimens gave higher values of compressive strength than the neat blended cement paste specimens. On immersing the neat blended cement specimens and polymer impregnated specimens especially that irradiated at 30 kGy in seawater and different concentrations of magnesium sulfate solutions up to 6 months of curing, the results showed that the polymer impregnated blended cement (OPC-RHA-UPE) paste have a good resistance towards aggressive media as compared to the neat blended cement (OPC-RHA) paste. The results also indicated that the sea water has a greater corrosive effect than the magnesium sulfate solutions. These results were confirmed by scanning electron microscopy (SEM) and mercury intrusion porosimetry (MIP).

Keywords: Blended cement paste, polymer-impregnated cement composite, gamma-irradiation, magnesium sulfate solutions, seawater, mercury intrusion porosimetry.

INTRODUCTION
The construction industry increasingly requires products that are cost effective and easy to use, to enable fast track application whilst achieving a high physical performance. Because of this fact, the types and quantities of cement
production have been increased all over the world. Blended cements are types of cements containing additive rather than used in ordinary Portland cement, which have considerable scientific and technological interest, because such addition increases the chemical resistance to sulfate attack, impermeability, lowering heat of hydration of cement and thermal expansion of the hydrated cement pastes. In addition, incorporating a polymer in cementitious mix brings key advantages, particularly in terms of workability, abrasion, bond strength, adhesion with substrates, or waterproofing properties of mortars and concretes. The application of polymer on concrete has significantly progressed in the past 50 years. Polymer-impregnated concrete provides definite advantages over conventional concrete on strength and durability by improving concrete pore structure.

Aggressive attack of sulfate ions present in soil, ground water, and seawater is one of the factors responsible for damage and deterioration of Portland cement concrete. These have been numerous field studies on the distress caused to concrete structures generated by sulfate attack. Sulfate attack has often been discussed in terms of the reaction between the hydrates in cement pastes and the dissolved compounds, such as sodium sulfate or magnesium sulfate, in the attacking solution, leading to the formation of Mg-containing hydrates (M-S-H) gel, as well as gypsum and thaumastic. Recently, there has been a growing trend towards the use of supplementary cementitious materials, whether, natural wastes, or by-products, in the products of blended cements because of ecological, economical and diversified production.

Two different types of lignite fly ashes and two natural pozzolans have used for the production of 13 blended cement mortars. All the specimens immersed in 5% sodium sulfate solution for 24 months. The results showed that the addition of pozzolanic admixture in most cases had a positive effect on the sulfate resistance. In addition, the carbonation depth in all blended mortars was greater than that in Portland cement mortar. Binici and Aksogan studied the sulfate resistance of blended cements containing a high volume of ground granulated blast-furnace slag (GGBS) and natural pozzolana (NP) by exposure to 5% magnesium sulfate and 5% sodium sulfate solutions. Portland cement-based materials subjected to attack from external sulfates may suffer from two types of damage: loss of strength of the matrix due to degradation of C-S-H, and volumetric expansion leading to cracking. Expansion, which leads to cracking, attributed to formation of expansive compounds such as ettringite;
proposed the cause of damage to be due to the formation of gypsum crystals. The effect of marine environment on concrete specimens made with different plants (ASTM I, II and V) and blended cements incorporation different percentages of volcanic ash (VA) up to 30% was also studied \cite{18}; the specimens were exposed to marine environment for a period of one year.

The effect of silica fume on deterioration resistance to sulfate attack in seawater within tidal zone and simulated wetting-drying condition has been studied in Portland cement pastes containing silica fume (SF) with/without ground granulated blast-furnace slag (GGBS). Changes in the compressive strength and capillary water absorption of specimens as a function of silica fume content have been investigated. The results showed that the strength change factors of specimens with SF were greater than that of the mixtures without SF \cite{19-20}.

The scope of this paper aims to attempt the evaluation and performance of the neat blended and polymer-impregnated blended cement composites towards aggressive sulfate solutions and seawater.

**MATERIALS AND EXPERIMENTS**

**Materials**

A freshly produced sample of ordinary Portland cement (OPC) obtained from the National Cement Company (Egypt) was used. Rice husk ash (RHA) obtained by the burning of rice husk at a temperature of 700°C for an interval increment time 2h. The chemical oxide composition of OPC and RHA used in this investigation are shown in Table 1.

<table>
<thead>
<tr>
<th>Table (1): Chemical oxide composition of OPC and RHA</th>
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<tr>
<td>OPC</td>
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<tr>
<td>SiO$_2$ (%)</td>
</tr>
<tr>
<td>Al$_2$O$_3$ (%)</td>
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<tr>
<td>Fe$_2$O$_3$ (%)</td>
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<tr>
<td>CaO (%)</td>
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<td>MgO (%)</td>
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<td>SO$_3$ (%)</td>
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<td>K$_2$O (%)</td>
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<td>Na$_2$O (%)</td>
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<td>Loss on ignition</td>
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The unsaturated polyester resin (UPE) used in this investigation is a general-purpose resin and contains 40% styrene monomer. It was supplied by Saudi Industrial Resins Company (SIR)
Ltd., Jeddah and commercially sold under the name Sirpol 8230. It has a viscosity 450 cP and a specific gravity of 1.08 g/cm$^3$ at 25°C.

**Samples preparation**

The hardened blended cement paste was prepared by the partial substitution of ordinary Portland cement (OPC) with 5% rice husk ash (RHA) and it was designated as OPC-RHA. The standard (optimum) water of consistency was used. The resulting paste was moulded into cubic specimens by using cubic moulds (each edge 2.5cm in length). The moulds with the specimens placed at 100% relative humidity for the first 24h at 25°C. Then the specimens were demoulded and cured under tap water for an additional 6 days.

**Impregnation and polymerization**

The hardened specimens of the blended cement pastes after 7 days of hydration, were dried at 105°C after stopping of the hydration and then impregnated with unsaturated polyester resin (UPE) for 3hr. in the impregnation unit. The polymer-impregnated specimens were irradiated from 10 to 50 kGy of gamma rays using Co-60 gamma cell-220 source (made in India). The impregnated specimens are designated as (OPC-RHA-UPE).

**Curing in aggressive media**

The aggressive media used in this study were seawater and aqueous solutions of magnesium sulfate having different concentrations of 1, 3, and 5% by weight. Both of the hardened blended cement specimens, and polymer-impregnated ones, which irradiated at 30 kGy were immersed in these aggressive solutions for extra time intervals 7, 28, 60, 90 and 180 days. Tap water was used as a reference solution for comparison.

**Physico-mechanical measurements**

Physico-mechanical measurements were carried out on the hardened specimens of the blended cement paste as well as the polymer-impregnated specimens irradiated at 30 kGy using standard procedures. Scanning electron microscopy (SEM) and mercury intrusion porosity (MIP) were applied to investigate the microstructure of those specimens. The deterioration of the cubic specimens was investigated by determining the loss of compressive strength (LCS) which is calculated as follows:

\[
\text{Loss of compressive strength LCS (\%) = } \frac{(A-B)}{A} \times 100
\]

Where:
A is the average compressive strength of specimens cured in tap water and B is the average compressive strength of specimens immersed in the test solutions for the same period.

RESULTS AND DISCUSSION

Effect of irradiation dose on compressive strength

Cross-linking is the most important effect of polymer irradiation because it can usually improve the mechanical, thermal and chemical environmental properties of preformed parts as well as bulk materials. Both polymer cross-linking and degradation by chain scission occur during treatment, but one or the other of these effects may be predominant in some materials \([21]\). The results of compressive strength for hardened blended cement paste impregnated with unsaturated polyester resin as a function of gamma-irradiation doses showed in Fig. 1 they indicated that the compressive strength of the composite material increases gradually with increasing of the irradiation dose. This mainly attributed to an increase of the number of cross-linking of the polymeric chains under the effect of irradiation dose leading to the formation of a network structure. In addition to, the interaction between calcium silicate hydrate formed during the hydration reaction of the blended cement and the polymer present in the pores during irradiation polymerization, \([22-24]\) that enhanced the interphase bonding, and as a result, an improvement of the mechanical strength of the specimens takes place. Also, the deposition of the polymeric material in the residual pore system of the impregnated specimens resulting in further improvement in the mechanical properties of the impregnated specimens as compared to the un-impregnated specimens.

Effect of aggressive media

Compressive strength

The relation between compressive strength values of neat blended cement (OPC-RHA) paste as a function of immersion time (days) are shown in Fig.2. It observed that the compressive strength values of the hardened blended cement paste immersed in seawater and different concentrations of magnesium sulfate solutions decrease slightly with increasing immersion time. This mainly attributed to the utilization of a supplementary cementing material, (rice husk ash) which consumes the deleterious CH (Portlandite), and dilutes the C\(_3\)A phase due to a reduction in the quantity of cement \([7]\). For a given immersion time, the results showed that the neat blended cement specimens are more susceptible to the deleterious seawater environment than that to the magnesium
sulfate solutions. This behaviour may be due to the fact that, seawater contains both sulfate and chloride ions leading to more degradation of C-S-H, as well as the volumetric expansion occurred due to the formation of expansive compounds such as ettringite phase and chloro aluminate hydrates. Meanwhile, the results of Fig.3 indicated that the compressive strength values of polymer-impregnated blended cement (OPC-RHA-UPE) paste are very slightly decrease as compared to those of the neat blended cement paste specimens. This related directly to the cross-linking of polymeric material that formed under the effect of gamma-irradiation, which increases the solid part within the pore system leading to a significant reduction of the total pore volume and a sort of discontinuity of the pore system. In addition, the presence of polymeric material prevents the contact between aggressive solutions and the hydrated products and consequently minimizes the damage effect of the aggressive media.

Fig.(1): Effect of irradiation dose on compressive strength values for the impregnated blended cement paste
Fig.(2): Compressive strength of the neat hardened blended cement (OPC-RHA) paste soaked in different concentrations of magnesium sulfate solutions and sea water for various time intervals.

Fig.(3): Compressive strength of the polymer impregnated blended cement (OPC-RHA-UPE) paste soaked in different concentrations of magnesium sulfate solutions and sea water for various time intervals.
Loss of compressive strength (LCS, %)

The percentage of compressive strength loss of both neat and polymer impregnated blended cement pastes after soaking in seawater and different concentrations of magnesium sulfate solutions for various immersion time intervals (7-180 days) showed in Figs. 4, 5 respectively. The results indicated that the compressive strength loss of both two types of specimens increases with the increase of the concentration of magnesium sulfate solutions as well as the increase of immersion time. This behaviour is due to the same reasons mentioned earlier. For a given immersion time, seawater has a greater corrosive effect on the specimens than that of magnesium sulfate solutions. On comparison of the results it can be observed that, the loss of compressive strength (LCS, %) of polymer-impregnated blended cement paste after 180 days immersion in the different aggressive solutions are 0.175, 0.212, 0.509 and 0.702 % for the different concentrations of magnesium sulfate solutions of 1%, 3%, 5% and seawater, respectively. Whereas, the values of loss of compressive strength (LCS, %) of the neat blended cement paste immersed under the same conditions are 0.776, 1.585, 2.146 and 2.851%, respectively. This explains the marked resistance of the polymer-impregnated specimens towards aggressive media and the consequent extended durability of these OPC-RHA-UPE specimens.

Fig.(4): Loss of compressive strength of the neat hardened blended cement (OPC-RHA) paste soaked in different concentrations of magnesium sulfate solutions and sea water for various time intervals.
The variations of the water absorption values of the neat blended cement paste as a function of the immersion time as well as the different concentrations of magnesium sulfate solutions and seawater showed in Fig. 6. The results showed that the water absorption percentages increase with increasing concentrations of magnesium sulfate solutions as well as the increase in the immersion time. For a given immersion time, the water absorption percentage of neat specimens immersed in seawater are higher as compared to the values obtained after soaking in magnesium sulfate solutions. This effect is attributed to the partial disintegration of some of the hydration products in the pores of the specimens to the extent that slight expansion and little cracks of the specimens occurred which, enhanced by the formation of expansive phases (ettringite) with the extra-formation of chloro aluminate hydrates in case of immersion in sea water. On the other side, the data obtained of water absorption percentage in the case of polymer-impregnated blended cement, (OPC-RHA-UPE) paste Fig. 7 showed that, the rates of water absorption percentage obtained for the polymer-impregnated specimens are lower than that of the neat blended cement specimens. This is mainly due to the presence of polymeric materials

Water absorption (%)
within the residual pore system, which prevents the contact of aggressive solutions with the hydrated cement constituents.

Fig. (6): Water absorption of the neat hardened blended cement (OPC-RHA) paste soaked in different concentrations of magnesium sulfate solutions and sea water for various time intervals.

Fig. (7): Water absorption of the polymer impregnated blended cement (OPC- RHA - UPE) paste soaked in different concentrations of magnesium sulfate solutions and sea water for various time intervals.
Morphology and microstructure

The microstructure of the hardened blended cement paste made of OPC-RHA (neat) and cured in tap water for 7 days of hydration showed in Fig. 8(a); the micrograph showed a dense structure of platelet-like and crumpled foils of C-S-H phase as well as calcium hydroxide which appeared as small hexagonal crystals. While, curing of the hardened blended OPC-RHA cement pastes in 5% MgSO₄ solution and seawater for 180 days; after curing in tap water for 7 days results in the formation of well crystallized hydrates of calcium silicate hydrates (C-S-H), ettringite (C₃A₃CaSO₄·32H₂O) and monosulfate (C₃A.CaO·12H₂O) hydrates. The latter hydrates appeared as a rod-like crystals and large hexagonal crystals in the microstructure shown in Fig. 8 (b & c). The formation of rod-like (well crystallized) ettringite crystals as well as the large hexagonal crystals of monosulfate hydrate leads to an opening of pore system that is associated with some reduction in the mechanical properties of the neat OPC-RHA paste when exposed to aggressive media. In addition, scanning electron microscopic (SEM) examination of the hardened blended (OPC-RHA) paste after 28 days of hydration and impregnated with UPE polymer followed by gamma-irradiation at 30kGy leads to the results showed in Fig. 8d these results displayed that; the UPE polymer particles filled the pores of the specimens and form a thin layer over the hydrated products in the pore system. This is associated with enhancement of the mechanical properties of the OPC-RHA-UPE specimens cured in tap water Fig. 8(d). The micrographs in Fig.8 (e & f) clearly indicate that, the presence of polymeric material within the pore system of the OPC-RHA-UPE composite specimens exhibiting greater resistance to aggressive solutions than the neat specimens at the same immersion time.
Fig. (8) Scanning electron micrographs of the neat blended cement (OPC-RHA) pastes immersed in: tap water (a), 5% magnesium sulfate solution (b) and sea water (c) after 6 months and polymer impregnated blended cement(OPC-RHA-UPE) paste cured in: tap water (d), 5% magnesium sulfate solution (e) and sea water (f) under the same conditions
Mercury intrusion porosimetry (MIP)

In order to estimate the pore size distribution of porous solid materials, mercury intrusion porosimetry (MIP) as one of the main methods of investigation is used. Figure 9 represents the relation between cumulative intruded pore volume of blended cement (OPC-RHA) paste as a function of pore diameter. It demonstrated that, the neat blended cement (OPC-RHA) specimens cured in tape water for 180 days has a lower cumulative intruded pore volume than the same specimens immersed in 5% magnesium sulfate solution and seawater for 180 days. This may be ascribed to the fact that the presence of active RHA results in a hydration interaction with Ca(OH)$_2$, liberated during the hydration process of OPC clinker, and yields addition amounts of calcium silicate hydrate (C-S-H) gel. Therefore, the pore volume in the OPC-RHA specimens would be filled with the additional hydrated product (C-S-H); this is leading to a decrease in the porosity of the neat OPC-RHA paste when cured in tap water for 180 days. As a result, the cumulative intruded pore volume becomes much less; so, the opportunity of mercury intrusion into the pore system becomes difficult. On the other hand, there is a sort of crack occurs under the aggressive effect of magnesium sulfate and seawater; this accompanied with an opening in the pore system leading to an increase in the porosity. As a result, the values of the cumulative intruded pore volume become much higher for the specimens immersed in the aggressive media of magnesium sulfate and seawater. Also, Fig. 10 illustrated that the values of the cumulative intruded pore volume of the polymer-impregnated blended cement (OPC-RHA-UPE) specimens immersed in tap water, 5% magnesium sulfate solution and seawater for 180 days, have lower values as compared to those of the neat blended cement pastes (OPC-RHA) specimens under the same conditions. This may be attributed to the presence of polymeric materials formed under the effect of gamma- irradiation inside the porous system which has two functions; decreasing of the porous system as well as it protection the hydrated products against aggressive attack; as a result, the intrusion of mercury towards the limited pore size and the discontinuous pore
Fig. (9): Cumulative intruded pore volume as a function of pore diameter of the blended cement (OPC-RHA) paste soaked in tap water, 5% magnesium sulfate solution, and sea water for 6 months.

Fig. (10): Cumulative intruded pore volume as a function of pore diameter of the polymer impregnated blended cement (OPC-RHA-UPE) paste irradiated at 30kGy; immersed in tap water, 5% magnesium sulfate solution, and sea water for 6 months.
CONCLUSION

The following conclusions can be drawn based on the test results of this study:

The partial substitution of ordinary Portland cement by active pozzolanic materials such as rice husk ash (RHA), 5% by weight, increased the resistance of the neat blended cement pastes towards aggressive media.

Polymer-impregnated blended cement [OPC-RHA-UPE] paste and subjected to 30 kGy of gamma rays has a greater resistance towards the aggressive media than that of the neat blended cement OPC-RHA paste.

Mercury intrusion porosimetry (MIP) and scanning electron microscopy (SEM) confirmed that, the polymer-impregnated specimens under the effect of gamma-irradiation showed lower porosity, lower loss of compressive strength (LCS,%) and high resistance to sulfate attack than those of the neat blended cement specimens cured under the same conditions.

REFERENCES


مجلة البحوث الإشعاعية والعلوم التطبيقية
مجلد 3 عد 3(أ) ص ص 791- 808 (2010)

قدرة تحمل عجائن الأسمنت المخلوطة المشربة بالبوليمير والمشعة بأشعة جاما
مجدى منصور محمد، هدى علي عبد الرحمن، مها محمد يونس
قسم كيمياء الإشعاع - المركز القومي للبحوث تكنولوجيا الإشعاع 3، أحمد الزمر، حي الزهرة، مدينة نصر، القاهرة، 09.06.10.

تلقى هذه الدراسة الضوء على قدرة تحمل وفاعليّة عجينة الأسمنت المخلوطة الخالصة وكذلك العجينة المشربة بالبوليمير تجة ماء البحر والتركيزات المختلفة من محاليل كبريتات الماغنسيوم لفترات زمنية مختلفة تصل إلى 6 أشهر. وقد تم تحضير عينات من عجينة الأسمنت المخلوطة الخالصة من خلال استبدال 5% من الأسمنت البورترلاني العادي بقشر الأرز المحروق والذي يحتوي على السيليكا النشطة ووضعت هذه العينات تحت ماء الجفيف لمدة 7 أيام. وبالمثل تم تحضير عجينة مماثلة وتشيرها بالبوللي أستر الغير مشبع وتعريضها لجرعات إشعاعية مختلفة من أشعة جاما تتراوح بين 10 – 50 كيلوجرامات.

وقد أوضحت النتائج أن العينات المشربة بالبوليمير والمشعة أعطت قيم أعلى في قوة تحمل الضغط الميكانيكي عن العينات الخالصة التي لا تحتوي على البوليمير. وقد غمر كل من عينات الخالصة وكذلك المشربة بالبوليمير والمشعة بجرعة إشعاعية مقدارها 30 كيلوجرام في ماء البحر ومحاليل كبريتات الماغنسيوم ذات التركيزات المختلفة لفترات زمنية تصل إلى 6 أشهر، فقد لاتنتج على أن العجينة المشربة بالبوليمير والمشعة أظهرت مقاومة جيدة تجاه الأوساط الشديدة بعجينة الأسمنت الخالصة التي لا تحتوي على البوليمير. كما أظهرت الدراسة أن ماء البحر له تأثير تأكيد أشد من محاليل كبريتات الماغنسيوم، وقد تم تأكيد هذه النتائج عن طريق ألسنين الألكتروني الميكروسكوبية وقياس المسامية.