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Probing sulphur speciation in sea water exposed concretes using Raman spectroscopy

M. Premila

Materials Science Group, Indira Gandhi Centre for Atomic Research, Kalpakkam Tamilnadu 603102, India premila@igcar.gov.in

¹R. Rajaraman, ⁴U. Sudha, ⁴Vinita Vishwakarma, ⁴D. Ramachandran, ²R.P. George, ³U. Kamachi Mudali and ¹G. Amarendra

¹Materials Science Group ²Metallurgy and Materials Group ³Materials Chemistry and Metal Fuel Cycle Group Indira Gandhi Centre for Atomic Research, HBNI, Kalpakkam – 603 102, India ⁴Centre for Nanoscience and Nanotechnology, Sathyabama University,Chennai – 600 119, India

ABSTRACT

Cooling water structures of nuclear reactors are continuously being exposed to harsh marine environment leading to corrosion induced damage. Flyash reinforced concretes (FA) are known to possess better resistance to corrosion as compared to normal concrete. Further improvement in corrosion resistance is brought about by selective nano phase modification of FA using nano titania (FAT), nano calcium carbonate (FAC) and a mixture of both (FATC). The present study is aimed at following the microstructural changes in FA and nanophase modified FA associated with prolonged sea water exposure (SWE) using Raman and Infrared (IR) spectroscopy. IR on 365 days SWE concrete samples revealed a structural modification of both FAC and FATC, while FAT and FA were relatively unaffected. FAC, FAT and FATC revealed the presence of elemental sulphur on their surface, marking the onset of bio deterioration in concrete. Such clusters of sulphur are absent in FA indicating that all the sulphur formed has been oxidised by sulphur oxidizing bacteria to sulphuric acid, leading to extensive biodegradation. Thus nanophase modification has improved biocorrosion

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resistance of FA. Among the studied concretes, FATC is observed to exhibit superior bio corrosion resistance, although it also undergoes a structural modification on SWE. *Keywords: Fly ash concrete, nanophase modification, biodeterioration, Raman Spectroscopy, FTIR*

INTRODUCTION

Concrete structures of nuclear reactors using sea water as coolant are continuously being exposed to harsh marine environment. This leads to extensive biochemical corrosion induced damage of these structures. Improving resistance of concrete against bio deterioration is one of the important aspects in long term reactor operations. Flyash reinforced concretes (FA) are known to possess better resistance to corrosion in view of their superior mechanical strength as compared to normal concrete (1-4). It is also reported that in contrast to normal concrete, FA exhibits exponential increase in its compressive strength on prolonged exposure to sea water due to increase in cementitious products (5,6). Nevertheless the use of high concentrations of flyash in concrete makes concrete prone to leaching and also affects the setting and initial strength development in concrete (7). Further improvement in corrosion resistance, especially under harsh marine environments, is being brought about by selective nano phase modification of FA (8). Related structural changes due to nanophase modification and changes on account of SWE provide important inputs in understanding concrete durability under harsh marine environments. Optical techniques, are ideally suited to study the associated microstructural changes of nanophase modified concrete upon SWE. In the present study both Raman and IR measurements have been carried out on flyash concrete (FA), flyash concrete reinforced with calcium carbonate nanoparticles (FAC), with titania nanoparticles (FAT) and with both calcium carbonate and titania nanoparticles (FATC) on both as cast and 365 days sea water exposed samples to follow the structural modifications associated with prolonged SWE.

EXPERIMENTAL PROCEDURE

Four different types of concrete– FA concrete (FA), FA with 2% TiO₂ nanoparticles (FAT) FA, with 2% nano CaCO₃ (FAC), FA with 2% 1:1 mix of nano TiO₂ and nano CaCO₃ (FATC) have been cast according to IS 8112:1989 f. The total content of all the materials (cement, FA and nanoparticles) for all the mixes was 375Kg/m³. The water to powder ratio was maintained at 0.44. Further details of preparation procedure was reported in our earlier work (8). All specimens were demoulded after 24 hours of casting and the samples were cured for 28 days in normal fresh water. These samples have been exposed to sea water at the Nuclear Desalination Demonstration Plant (NDDP) pump house sump and withdrawn after 365 days.

Raman spectroscopic measurements were carried out using Renishaw InVia micro-Raman spectrometer (Renishaw, UK) equipped with 514.5 nm Ar ion laser, 2400l/mm grating and peltier cooled CCD detector, giving a spectral resolution of 2 cm⁻¹. Acquired spectra were corrected for Rayleigh scattering and normalised to total area for quantitative comparisons. Selected peak regions were fitted with mixed Gaussian functions using WIRE software (Renishaw, UK).

IR measurements were carried out using Bruker make (Model- Vertex 80V) FTIR spectrophotometer in the range 400-5000 cm⁻¹ with a resolution of 4 cm⁻¹ using a combination of globar source, KBr beam splitter and DLaTGS detector. Measurements were done on powdered samples dispersed in KBr matrix in the transmission mode.

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RESULTS AND DISCUSSIONS

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Fig 1 shows the Infrared (IR) of as cast 28 days cured FA concrete along with FAT, FAC and FATC. IR measurements revealed expected phonon features for FA concrete. The most intense feature at 1091 cm⁻¹ corresponds to the Si-O stretching frequency of the major cementitious product – the C-S-H gel. The mode at 462 cm⁻¹ can also be attributed to the Si-O bending mode of the C-S-H gel, while the mode at 1464 cm⁻¹ arises due to the C-O stretching of the carbonate species in the concrete. The absence of a sharp features at 354 cm⁻¹ and 3616 cm⁻¹ characteristic of Portlandite (crystalline Ca(OH)₂ - the major hydration product of OPC concrete) in FA concrete provides excellent proof of the fact that flyash in FA concrete reacts with excess Ca(OH)₂ producing additional cementitious products that helps improve the mechanical strength of normal concrete (9). Further the IR spectra of all the four concrete samples are identical (Fig1) irrespective of the type of nanoparticle substitution implying that the overall structure of all the four concrete samples remains unaffected on nano particle substitution. Raman spectroscopy on these concrete samples is subject to high florescence backgrounds, thus obscuring most of the Raman signals. Fig 2 shows a representative Raman spectrum of the FATC sample along with the Raman spectra of nano titania and nano CaCO₃. A mode at 462 cm⁻¹ appears in the Raman spectra of FA, FAC, FAT and FATC (Figures not shown) and is characteristic of the Si-O mode of the C-S-H gel.

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Fig.2. Raman spectrum of FATC along with the starting materials CaCO₃ and TiO₂

IR - 365 DAYS EXPOSED SAMPLES



Fig. 3. Area normalized set of IR spectra of the as cast unexposed (solid lines) along with the 365 days sea water exposed (dash-dot lines) FA and FATC samples

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Fig 3 shows the area normalized set of IR spectra of the as cast unexposed samples (FA and FATC) along with the 365 days sea water exposed (SWE) samples. It can be observed from the figure that FA and FAT (not shown in Fig. 3) concrete samples remain more or less unaffected even after 365 days of exposure to sea water, while FAC (not shown in Fig 3) and FATC show marked changes as compared to the corresponding unexposed samples. In particular, the intensity of the major C-S-H mode at 1096 cm⁻¹ is drastically reduced while the shoulder at 1020 cm⁻¹ evidently picks up on sea water exposure. This clearly indicates a change in the C/S ratio of the C-S-H gel that could have caused the above shift in C-S-H modes (9). It is also very surprising to note that the modified structure of both FAC and FATC samples after 365days of SWE are identical (figure not included). Since both FAC and FATC contain CaCO₃, we immediately infer that the observed structural change on SWE could be associated with polymorphic transformations of CaCO₃ (9).



RAMAN – 365 DAYS EXPOSED SAMPLES

Fig.4. Raman spectrum of SWE FATC showing sharp features characteristic of elemental sulphur

Raman spectra collected at random spots of the SWE samples do show any major changes as compared to unexposed samples. However, it is interesting to note that sea water exposed FAC, FAT and FATC revealed white micron sized particulates in clusters on the surface of the nanophase modified concrete (Inset Fig. 4). Raman spectra of these particulates, as shown in Fig. 4, revealed sharp well defined intense peaks at 153, 219 and 472 cm⁻¹, indicative of presence of elemental sulphur (10). Sea water contains appreciable amounts of suphate that attacks concrete and on reaction with iron in concrete forms FeS_2/H_2S on the surface. Elemental sulphur is a byproduct got in large amounts during bio oxidation of pyrites in acidic medium (10). Micro organisms like sulphur oxidizing bacteria (SOM) oxidizes the elemental sulphur (S⁰) to sulphates – SO_4^{2-} and then subsequently to H_2SO_4 . This acid then leaches out the surface of the concrete – known as bioleaching (10). The fact that such clusters of sulphur are absent in FA indicates that all the sulphur formed on surface of FA has been entirely consumed/attacked by SOM converting it to sulphuric acid and that FA is in an advanced stage of bioleaching (10). Meanwhile for the same period of exposure, the presence of elemental sulphur on the surfaces of nanophase modified FA concrete

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(FAC, FAT and FATC) indicates only an initial stage of bioleaching. In addition, the presence of sharp well defined satellite peaks at 186, 247 and 437 cm⁻¹ along with main modes (marked as asterix in Fig 4) is indicative of a structural transformation of sulphur that occurs just before the onset of bio-oxidation of sulphur to sulphate by SOM (10).

In order to follow the evolution of the 247and 437 cm⁻¹ features (which could indicate the extent of onset of bio corrosion) - area normalization of Raman spectra of all the SWE samples was carried out. The area under the peaks (247 and 437 cm⁻¹) were followed for FAC, FAT and FATC. It was found that the area of both the peaks exhibited a systematic decrease in the following order FAC > FAT > FATC (Fig5) implying that the addition of nano TiO₂ has indeed served to decrease the extent of attack as compared to FAC. FATC thus is observed to exhibit superior resistance to microbial attack as compared to even FAT.



Fig.5. Variation of normalized area under the satellite peaks at 247 and 437 cm⁻¹ for different compositions indicating the extent of biocorrosion

CONCLUSIONS

IR measurements on 365 days SWE concrete samples revealed a structural modification for both FAC and FATC concrete samples, while FAT and FA concretes were relatively unaffected as compared to the unexposed samples. This modification is attributed to occur on account of the presence of CaCO₃ in both FAC and FATC that could have undergone a polymorphic transformation on SWE. Using Raman spectroscopy we have obtained direct evidence for the first time, of the

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presence of elemental sulphur on surfaces of nanophase modified 365 days SWE, FAC, FAT and FATC samples, while such clusters are absent in 365 days SWE FA concrete. Detailed analysis of the normalized area of the sulphur peaks revealed that among the nanophase modified concrete samples FATC exhibited superior resistance to microbial attack under harsh marine environments. This is inspite of the fact that FATC has undergone a structural change on account of prolonged SWE. The presence of nano titania in the FATC matrix has served to inhibit bio corrosion. The present work thus provides excellent and direct proof not only of the fact that nanophase modification of FA concrete indeed improves resistance to bio degradation, but also clearly indicates that among all the studied concretes FATC exhibits superior resistance to microbial attack in harsh marine environments.

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