MICROSTRUCTURAL ANALYSIS OF BLENDED CEMENT CONCRETE IN MARINE ENVIRONMENT

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ABSTRACT

In all over the world, concrete is the most commonly used construction material. It is generally recognized that the environmental degradation of the concrete infrastructure is a serious, large scale and costly problem in many parts of the world. Although, considerable numbers of testing method are available to determine the various properties of concrete. But concrete researchers are trying to apply some advance technologies to analyse concrete. This study was carried out to develop an understanding of the performance of concrete in aggressive water made up of cements blended by pozzolanic materials like slag. X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) method have been used for the analysis of powder sample. In this research work we have analysed four samples of two different compositions (cement: slag=100:0 and cement: slag=70:30) and exposed of two different concentration 1N and 3N saline water. Concrete sample were exposed for 365 days in mentioned exposure condition. The study highlights the capabilities of the methods for the analysis of concrete towards the determination of hardened cement paste degradation behaviour of normal concrete and composite concrete exposed to same exposure. XRD results shows the presents of calcium carbonate and variation of silica for different samples. SEM/EDX analysis shows the morphological condition of the sample and elemental variation for different sample. XRD and SEM analysis ascertain the deterioration of concrete sample and experimental results reveals that composite concrete shows less deterioration than the normal concrete for the same exposure condition.

Keywords: *Concrete, degradation, aggressive water, XRD, SEM/EDAX.*

1. INTRODUCTION

To determine different properties many conventional or destructive testing (DT) methods are available. But the conventional methods have some limitations like time consuming, laborious and complicated procedure. Another major limitation of conventional method is we can't reuse the same sample in those methods. To get rid of those limitations of conventional method many standard non-destructive testing method (NDT) are now available. Concrete researchers are trying to include some of the advance technologies in non-destructive testing method. X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) are two of them. XRD is used for the mineralogical analysis of concrete and SEM is used for the morphological observation surface analysis of concrete.

Deterioration of reinforced concrete (RC) structures has been one of the most extended lessons, taught to mankind. Huge amount of money is being spent annually in rehabilitation and repair of deteriorated RC structures. In US, as highlighted by Gannon et al. (1992), the expenditure was estimated to be more than U.S $20 billion and to be increasing at U.S $500 million per year (Gannon and Cady, 1992).

Use of supplementary cementitious materials (SCM) in concrete provides a sustainable and feasible solution to the durability problems in coastal areas. Replacements of OPC by the pozzolan will not only help in conservation of natural resources, but it will also contribute towards reducing pollution and energy. Results showed that in almost all cases, use of cements blended with pozzolanic materials resulted in an enhanced performance of the concrete (Khan, Anis and Ahmed, 2015)

Most of the onshore structures are constructed with normal carbon steel reinforcement due to it being economical compared to stainless steel or galvanic protection alternatives. As concrete bears a natural alkalinity, therefore, under normal condition, it creates a tightly adhering γ-Fe_2O_3 oxide film around the reinforcing steel that keeps it protected as long as this layer is sustained. Before the actual degradation of concrete and the air and moisture access to the reinforcement bars, the corrosion of reinforcement bar is driven up majorly due to carbonation and chloride attack, if present, (Verbeck, 1975) described as a unique and specific destroyer. This results in the loss of alkalinity in concrete around the reinforcement bars and also the destruction of passive layer of Fe_2O_3 leading to the initiation of actual corrosion. The volume of iron oxidation product, eventually, causes severe cracks in the concrete providing unavoidable path for oxygen and water, bridging the structure over the threshold of corrosion.

In these days of modern technologies, concrete researchers also trying to use sophisticated technologies for simplicity and accuracy in the analysis of concrete. But there is no standard procedure to perform the tests of concrete using those advance technologies. That's why the capabilities of those technologies still under consideration to many researchers and needs more investigation about those technologies. The main purpose of this experiment is to judge the capability of advance technologies like XRD and SEM in the concrete field as well as to compare the performance of OPC and Composite Cement under different exposure condition.

2. METHODOLOGY

For The principal advantage of XRD is that a qualitative or semiquantitative evaluation of mineralogy is generated. The SEM consists of an electron optical column which generates and focuses an electron beam over the specimen surface. The products of cement hydration is not only complex compositionally but also structurally. About 70 per cent of fully hydrated cement consists of C-S-H gel, 20 per cent calcium hydroxide, and the rest ettringite, calcium aluminate mono sulphate hydrate, unhydrated clinker residue and other minor constituents (Diamond, 1976). For the purpose of study, various researches have been done. Mineralogical analysis has been carried out using XRD to determine what phases are present in concrete. Morphological analysis has been carried out to determine morphological condition of concrete using SEM.

2.1 Working Diagram

For conducting XRD and SEM tests four samples of two different compositions (cement: slag=100:0 and cement: slag=70:30) taken, which were exposed of two different concentration 1N and 3N saline water. The tests were performed at Bangladesh Atomic Energy Commission, Dhaka.

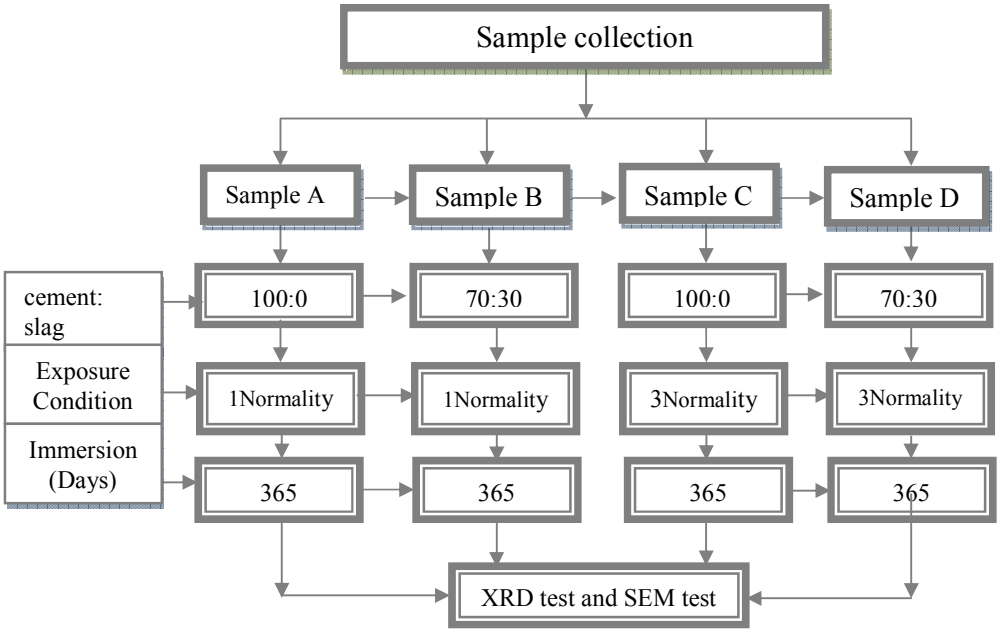

Figure 1: Flow diagram for investigation program.

2.1.1 X-ray Diffraction Analysis

In X-ray powder diffractometry, X-rays are generated within a sealed tube that is under vacuum. A current is applied that heats a filament within the tube, the higher the current the greater the number of electrons emitted from the filament. A high voltage, typically 15-60 kilovolts, is applied within the tube. This high voltage accelerates the electrons, which then hit a target, commonly made of copper. When these electrons hit the target, X-rays are produced. The wavelength of these X-rays is characteristic of that target. These X-rays are collimated and directed onto the sample, which has been ground to a fine powder (typically to produce particle sizes of less than 10 microns). A detector detects the X-ray signal; the signal is then processed either by a microprocessor or electronically, converting the signal to a count rate. When an X-ray beam hits a sample and is diffracted, we can measure the distances between the planes of the atoms mat constitute the sample by applying Bragg's Law. Bragg's Law is $\eta\lambda = 2\ d \sin\theta$, where the integer n is the order of the diffracted beam, *l* is the wavelength of the X-ray beam, d is the distance between adjacent planes of atoms (the d-spacing's), and θ is the angle of incidence of the X-ray beam. Since we know *l* and we can measure θ, we can calculate the d-spacing (Maroliya, 2012).

The sample was grinded and collected 53μm using standard meshing and the sample holder was filled with that sample. The sample holder size is 15mm×10mm×2mm. Then the top surface of sample holder was covered by a plexiglass which will level the top surface of specimen with sample holder. Then the sample holder is carefully placed into the diffractometer. Then the diffractometer was run and data was collected. For qualitative analysis of the data "X'Pert Highscore" software was used which was available with diffractometer. For quantitative analysis "X'Pert Plus" software was used which was also available with the diffractometer.

2.1.2 Scanning Electron Microscopy Analysis

To analyze the morphological evaluation of the samples, we used the scanning electron microscope (SEM) of type FEI Quanta Inspect S50, equipped with an EDX instruments spectrometer, INCA 200 soft.

First the powder sample was mixed thoroughly using a spatula. The powder sample was sprinkled lightly with a spatula and pressed slightly to seat and the sample was sprayed with a canned air to remove the loose grain from the top. Then it was coated to make the sample conductive. 20 nanometers Carbon coating material was used as it is cheap and almost invisible in most x-rays. Carbon at that thickness will have a little or no effect on elemental analysis. Then the coated sample was placed in the sample holder of 1 inch diameter of cylindrical mounts. After that, the sample holder placed in the sample chamber and the analysis carried out.

3. ILLUSTRATIONS

3.1 Table of XRD Analysis

XRD measurements were implemented on a Philips X'Pert diffractometer equipped with a figure ite monochromator using Cu Kα radiation and operating at 40 kV and 20 mA. Step scanning was performed with a scan speed of 2°/min and sampling interval of 0.02°/2θ. XRD was used to identify the hydrates in the cement pastes containing limestone powder.

Table 1: Pattern list of analysis of all samples

Sample Designation	Visible Chemical Formula	Reference Code	Compound Name
0S1N	SiO_2	01-086-1560	Quartz
	SiO_2	01-075-1381	Ceosite
	$CaCO_3$	01-072-1214	Calcite
30S1N	SiO_2	01-086-1560	Quartz
	Fe	01-087-0721	Iron
	$CaTiSiO_5$	01-085-0395	Titantite
	$Al_2Si_2O_5(OH)_4$	01-074-1786	Kaolinite-1
30S3N	SiO_2	01-086-1560	Quartz
	$CaCO_3$	01-072-1214	Calcite
	$Na(AlSi_3O_8)$	01-076-0898	Albite
0S3N	SiO_2	01-086-1560	Quartz
	$CaCO_3$	01-072-1214	Calcite
	TiO_2	01-088-1173	Rutile

In this section the percentage of various compounds in each sample from XRD analysis is shown in table. Amount of silica and calcite has increased with the increase in normality for the same ratio of slag and cement.

Table 2: Percentage of various compounds in different samples

Sample Name	Compound Name	Chemical Formula	Amount (%)
0SIN	quartz	SiO_2	91.38
	calcite	$CaCO_3$	8.63
0S3N	quartz	SiO_2	79.95
	rutile	TiO_2	6.03
	calcite	$CaCO_3$	14.02
30S1N	quartz	SiO_2	93.60
	iron	Fe	3.15
	titanite	$CaTiSiO_5$	2.37
	kaolinite	$Al_2Si_2O_5$	0.88
30S3N	quartz	SiO_2	84.36
	albite	$NaAlSi_3O_8$	6.01
	calcite	$CaCO_3$	9.63

3.2 Figures and Graphs

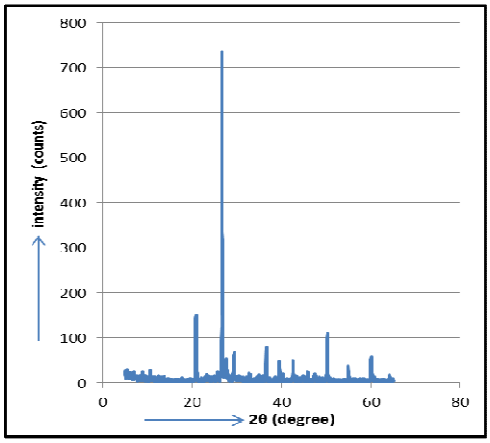

Figure 1: XRD diffractograms of sample-0S1N.

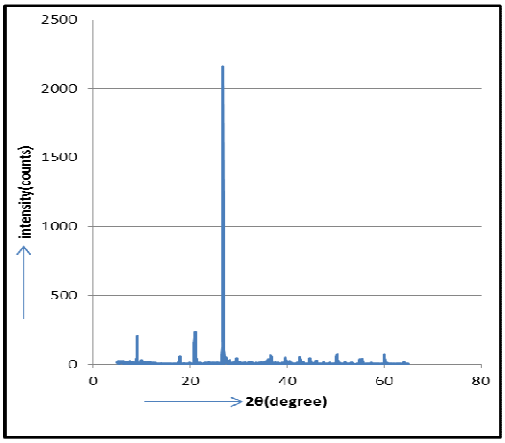

Figure 2: XRD diffractograms of sample-30S1N

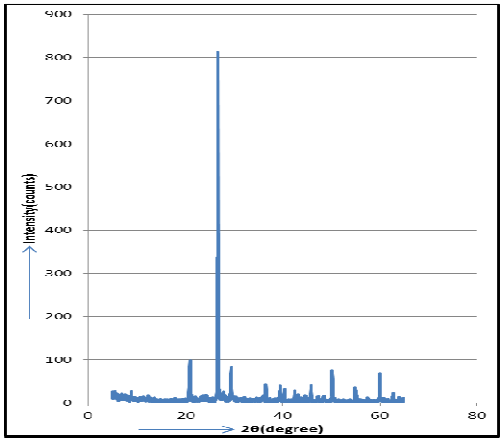

Figure 3: XRD diffractograms of sample-0s3N

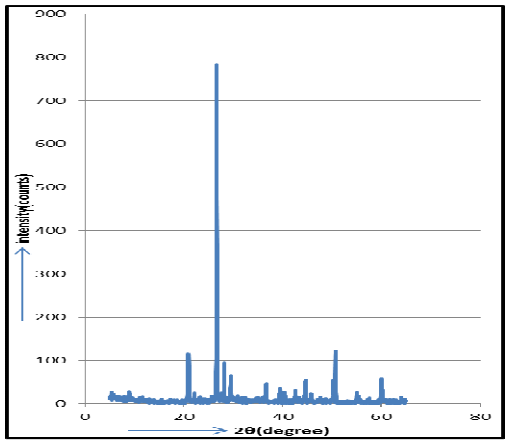

Figure 4: XRD diffractograms of sample-30S3N

Figure 1-4, represents the XRD diffractograms for investigated samples. Each figure presents the comparatively diffractograms of a sample taken from particular concrete block. The symbols on figures indicate the positions and peak intensities of powder diffraction.

In sample 0S1N figure 1, XRD analysis indicates predominance of quartz (SiO_2) peak at 26.73^0, 39.56^0, 55^0 and calcite ($CaCO_3$) also present at 29.48^0, 42.53^0. In sample 30S1N figure 2, XRD analysis shows the predominance of quartz (SiO_2) at 21^0, 26.73^0, 39.6^0 and 55^0. XRD analysis also shows peak for iron, titanite ($TiSiO_5$) and kaolinite ($Al_2Si_2O_5(OH)_4$) at 44.7^0, 27.36^0 and 9.98^0 respectively. For sample 0S1N figure 3, XRD analysis shows peaks for silica (SiO_2), calcite($CaCO_3$) and ruitle(TiO_2). The peaks of silica show at 21^0, 26.73^0, 55^0 and 60^0. Calcite and ruitle shows peaks at 29.48^0 and 28.03^0 respectively. Figure 4 of sample 30S3N, shows peaks of quartz, albite and calcite. Albite ($Na(AlSi_3O_8)$) and calcite shows predominance peaks at 28.07 and 29.48^0 respectively.

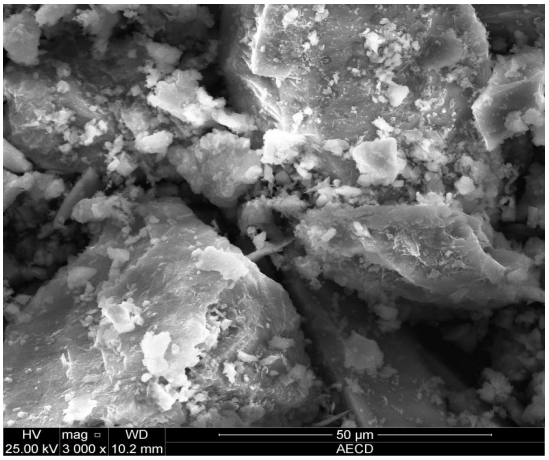

Figure 5**:** SEM image of sample 30S3N

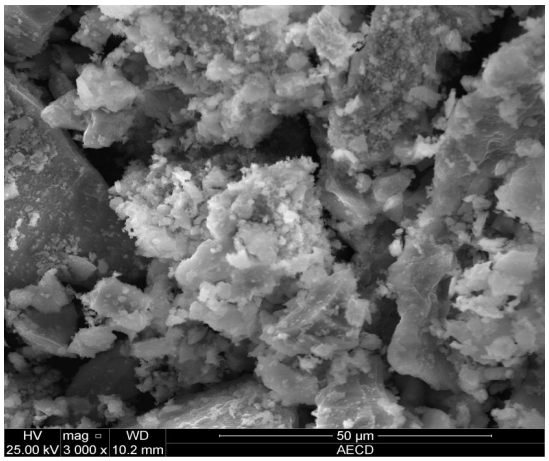

Figure 6**:** SEM image of sample 30S3N

SEM observation of sample 30S3N shows silica grain between the paste-aggregate interface and some amount of calcite crystal. Another important thing is that there is no specific sign of hydration products which is due to the leaching of $Ca(OH)_2$ in degradation. Cement paste has also break-down showing the distorted matrix of paste (figure-5 & 6).

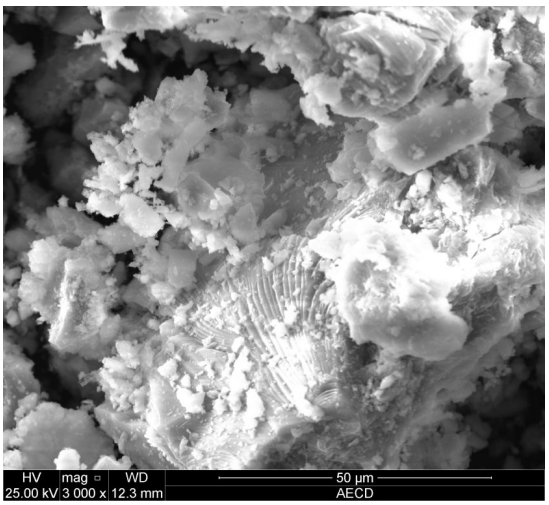

Figure 7**:** SEM image of sample 30S1N

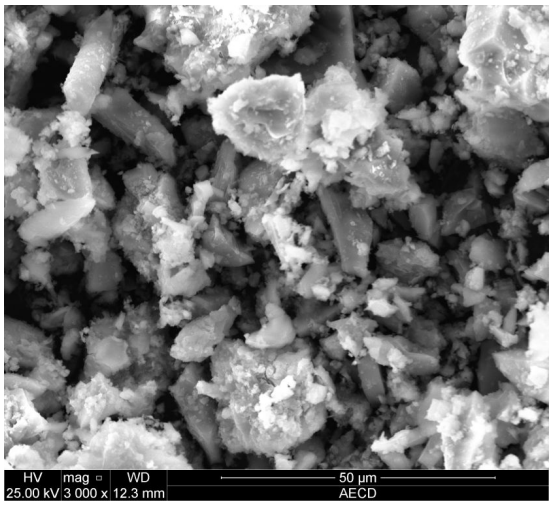

Figure 8**:** SEM image of sample 30S1N

SEM observation of sample 30S1N shows silica grain and hydration products like ettringite showing needle like structure (figure-8). In this case there is also leaching of cement paste but this sample shows some sort of compactness in the cement paste matrix (figure 7& 8).

4. CONCLUSIONS

The degradation of concrete depends on many factors. Some of the important factors of degradation are type of cement used, curing period, curing days, and exposure condition, exposure intensity etc. from the details discussion of the test results we can summarize the results and make some conclusions as follows.

Based on the XRD and SEM analysis and using the variables as stated above following conclusion can be drawn:

- Sample for same ratio of cement & slag shows less amount of silica and more amount of calcite with the increase of normality which means that concrete of same component shows more deterioration with sever environment.

- Sample for same exposure (normality) shows more amount of silica and less amount of calcite with the increase in percentage of slag which means that blended concrete shows more resistance to degradation than plain concrete when exposed to same environment.

- Blended concrete shows more compactness in cement matrix and hydration product in SEM image. But plain concrete shows distorted or breakdown cement paste matrix. These also give us idea about that blended concrete shows more resistance to deterioration.

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