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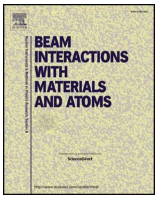

Characterization and application of automated in-vacuum PIXE/EBS system for direct analysis of chloride and sulfate ions attack in cementitious materials

M.S. Rihawy*, M. Alwazzeh, K. Abbas

Department of Chemistry, Atomic Energy Commission, P.O. Box 6091, Damascus, Syrian Arab Republic

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ABSTRACT

Ion beam analysis (IBA) techniques (Particle Induced X-ray Emission, PIXE and Elastic Backscattering Spectrometry, EBS), were applied to investigate chloride and sulfate ions diffusion into laboratory prepared mortar samples. Development and characterization of an automated in-vacuum macro PIXE/EBS system is thoroughly discussed. Depth profile information of both chloride and sulfate ions in laboratory prepared mortar samples, after immersion in sea water for nine months, was rapidly and easily obtained at fairly low cost and with standardless analysis, demonstrating the value of the application of IBA to elemental depth profiling in cementitious materials. Chloride and sulfate depth profiles were obtained for two sets of mortar samples, one prepared with different water/cement (W/C) ratios and the other with different sand/cement (S/C) ratios. Results showed higher diffusion rates of both chloride and sulfate ions when both ratios are increased. Additionally, the W/C ratio has a stronger influence in both sulfate and chloride penetration than the S/C ratio, and chloride ions penetrate faster than sulfates. Advantages and limitations of applying IBA techniques in this investigation are discussed. The comparison between PIXE and other X-ray based analytical techniques, namely X-ray fluorescence (XRF) and energy and wavelength dispersive X-rays (EDX/WDX), as well as other traditional wet chemical methods is reviewed, and industrial applications are discussed.

1. Introduction

Concrete structures are built with the intention of them lasting for a very long time. However, factors affecting the durability of concrete structures [1] (include extreme mechanical loading, chemical reactions, corrosion of reinforcement steel and temperature changes), can cause severe damage and even collapse of these structures.

Corrosion of steel in concrete is a major deterioration factor affecting the durability of reinforced concrete. It has been demonstrated that the presence of chloride ions in reinforced concrete, from de-icing salts or in marine environments is a main reason behind the occurrence of steel corrosion. When chloride ions penetrate reinforced concrete structures, the corrosion initiates in the presence of water and oxygen according to electrochemical mechanisms [2]. Additionally, the presence of sulfate salts either in the ground or mixing water or in saline environments considerably affects the durability of concrete according to known sulfate attack mechanisms [3,4]. As a result, combined attack of both chloride and sulfate ions found in marine environments causes severe deterioration to the concrete structures built in the sea or near the sea beaches.

The study of elemental content of cementitious materials is an important issue to provide useful information regarding the causes of failure of concrete. Traditional wet chemical analysis methods have been initially developed to perform elemental analysis of cementitious materials [5]. Subsequently, non-destructive, modern and faster techniques have been devised [6], particularly X-ray based techniques, namely X-ray fluorescence (XRF) and scanning electron microscopy (SEM) equipped with either energy dispersive X-ray (EDX) and/or wavelength dispersive X-ray (WDX) spectroscopy systems.

The use of ion beam analysis techniques (IBA) [7] has grown, mainly due to their non-destructive and multielemental characteristics. They can be used simultaneously to rapidly determine most elements in a sample with an accuracy (~5–10%) and sensitivity (μg/g), comparable to the XRF methods. In addition, easy sample preparation procedures are required to perform the analysis. Cementitious materials are well suited to ion beam analysis techniques. However, the scientific studies of elemental diffusion in cement-based materials applying IBA techniques are rather few [8–13], due to the lack of availability of accelerator machines. The recent development of IBA techniques and the spread of ion beam accelerators will strongly encourage researchers to

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* Corresponding author.
E-mail address: cscientific4@aec.org.sy (M.S. Rihawy).

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employ these powerful techniques as standard ones in this investigation.

Most previous IBA studies have utilized micro-beam or external beam systems, which are not necessarily available in many accelerator laboratories. The work presented here demonstrates the ability of conventional in-vacuum macro-beam (of mm size) system to perform chloride and sulfate depth profiling in cement based materials. Additionally, it describes a detailed characterization of in-vacuum chamber that has been developed to totally perform automated particle induced X-ray emission (PIXE) and elastic backscattering (EBS) measurements, together with the methodology applied to investigate both chloride and sulfate ions penetration profiles in cementitious materials. Advantages and limitations of IBA techniques in this investigation are discussed. Comprehensive comparison with other standard analytical methods is reviewed.

2. Experimental

2.1. Sample preparation

To verify the ability of our PIXE system to perform the evaluation of chloride and sulfate diffusion in cement based materials, simple pre-established mortar mixes were adopted. The sand used was crushed from the local dolomite rocks in Damascus suburb, which is widely used in concrete structures in Damascus. The commercially available ordinary Portland cement (OPC) was manufactured locally and its main composition can be found in [14]. The samples were prepared as follows. First, ordinary Portland cement (OPC) was dry-mixed with sand for two minutes, and then water was added and mixed continuously for three minutes. Samples were casted in cylindrical molds of 50 mm diameter and 100 mm height. Entrained air bubbles were removed by vibrating the samples for two minutes. Finally, they were left to dry for 24 h. Subsequently, they were unmolded and cured at 25 °C for a month. The characteristics of the concrete samples are tabulated in Table 1. Six different concrete mixtures were investigated in this work. They were classified in two groups to demonstrate the ability of PIXE system in the investigation of the effect of water to cement (W/C) and sand to cement (S/C) ratios on the diffusion of Cl and S into cement-based structures.

Directly after curing, large plastic containers were used to immerse in sea water (as the aggressive source of chloride and sulfate ions) during over nine months the prepared mortar samples. The sea water was brought directly from the Mediterranean Sea. Being immersed directly after curing assures that the mortar samples are water saturated and that the ions penetration process can be effectively governed by a diffusion process [15]. Subsequently, they were removed from sea water and let to dry for 10 days, then cut in a transverse direction to study the radial chloride and sulfate diffusion profiles in the exposed cross section (see Fig. 1). Finally, the samples surface was coated with a thin layer of carbon (less than 50 nm) to prevent local beam charging effects. Sequential beam spots, of area of $2 \times 2\,\mathrm{mm}^2$ each, across the sample from the center towards the edge are shown in Fig. 1. Two replicates were prepared and measured by PIXE in order to evaluate the error of the obtained concentrations.

Table 1
The characteristics of the prepared mortar samples.

	Sample code	Water to cement (W/C) ratio	Sand to cement (S/C) ratio
Group-1	W/C = 0.45	0.45	3
The effect of water to	W/C = 0.60	0.60	3
cement (W/C) ratio	W/C = 0.75	0.75	3
Group-2	S/C = 3	0.45	3
The effect of sand to	S/C = 4	0.45	4
cement (S/C) ratio	S/C = 5	0.45	5

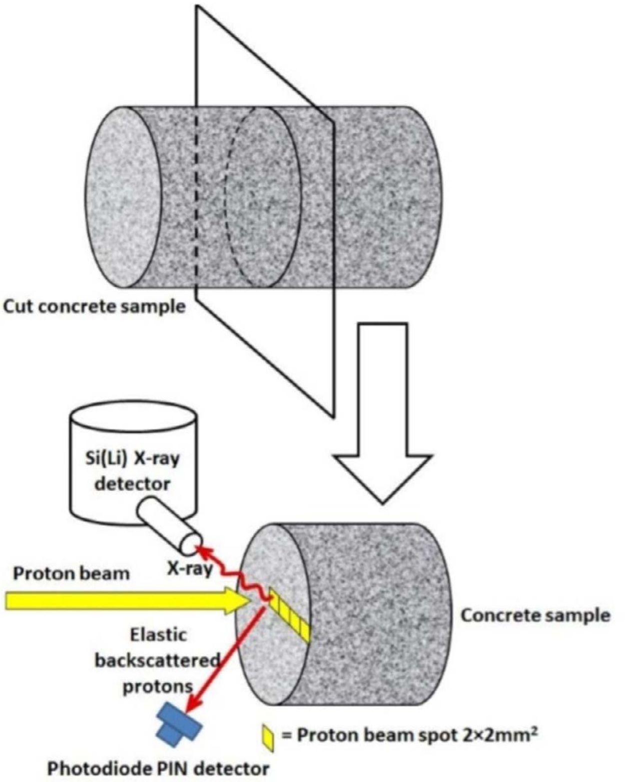

Fig. 1. Sketch diagram of the concrete sample cutting and the experimental setup of IBA analytical technique.

2.2. Instrumentation

Concrete samples were placed in-vacuum on a target holder, installed on a 2-axis (ϕ,Θ) automatic-controlled goniometer to both switch between irradiated samples by the beam and to control the incidence beam angle. Additionally, the goniometer controlling system can be operated at “patch mode” option, which enables examination of elemental concentrations profile across a surface of a sample by making automated step-by-step movement and acquiring the corresponding spectra at each step.

Using 1 MeV proton beam inhibits backscattered protons from arriving the Si(Li) crystal, (due to energy loss of protons that are totally stopped in the beryllium window of the detector), thus preventing degradation of the detector performance while maintaining efficiency for detecting low energy characteristic X-rays as the ones of Mg and Al. It also assures lower Bremsstrahlung background in the spectrum region of interest (S and Cl), enhances the S/Ca and Cl/Ca ratio yield (by circa 30% if a 2 MeV proton beam is considered, being Ca the most abundant element in the sample) then improving S and Cl detection limits and still maintaining fair sensitivity to detect major and minor elements up to Fe. All this shows that low energy accelerators can be successfully used in this type of study. Samples were irradiated with an incident beam normal to their surface with a beam current of 5 nA. A proton beam spot of 2 mm is typically obtained using two sets of beam collimators placed at the beam line. Samples can be moved horizontally in 2 mm steps across the beam from one edge to another, using the automatic-controlled goniometer (see Fig. 1). At each step, both induced X-rays and backscattered particles are collected simultaneously to obtain the required elemental depth profiles. The collected charge was 2 μC at each step, which requires about 5 min acquisition time.

A lithium drifted silicon detector (Si(Li) DSG type PGP-30-165) with