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Pulsed DC plasma as a tool for the generation of nanomaterials that mitigate the alkali-aggregate reaction in Portland cement concretes

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ABSTRACT

The efficacy of the pulsed DC plasma method in the mitigation of the aggregate alkali reaction, by the deposition of thin films of Al, Ti and Fe nanomaterials on potentially reactive aggregates was investigated from analytical techniques. These included field emission scanning electron microscope, X-ray dispersive energy microprobe, electron back-scatter diffraction, Raman and the resulting expansion in the modified accelerated mortar-bar method. In the 30 days of the test, the values of expansion were obtained in samples with *in nature* aggregates of (0.77 ± 0.03)% and in those treated of (0.16 ± 0.01)%, (0.16 ± 0.01)% and (0.16 ± 0.00)%, respectively.

1. Introduction

The durability of Portland cement concrete is defined as its capacity to resist weathering and mechanical wear agents or any other type of deterioration without losing its functionality and original properties. Water is the main factor in these degradations and is responsible for the decreases in its operational life [1–3].

In large engineering projects, such as hydroelectric dams, other factors can also decrease the operational lifetime of the project, such as multistressing, which is inherent in the structure and the multiple interfaces of the concrete with itself at joints between blocks and layers and with the water in the reservoir, soil, rock and atmospheric air. Other aggravating factors may be considered due to the need to use kneading water and local aggregates, when their contamination is not fully defined, affected by the geological history, composition, microstructure and the degree of alteration for dosing of the concrete. Thus, both water and the aggregates can potentially be reactive and generate chemical by-products in a reaction with the hydrates of the cement paste. This reactivity results in some mechanisms of deterioration, and pathological manifestations occur such as water percolation, leaching, dissolution or hydrolysis of components of the cement paste and of the aggregate itself, or the appearance of efflorescence, carbonation, chemical attacks by chloride, sulphate and other inorganic salts, volumetric expansions, cracks and structural ruptures, losses of mechanical strength and hardware corrosion [1,4–7].

In this context, the alkali-aggregate reaction, AAR, has been a global concern since its discovery in large engineering projects, as it is one of the main types of chemical attack on concrete that can unleash products with larger initial volumes than their reagents, which causes deleterious phenomena in the structures [8]. This process occurs primarily in dams, due to continuous contact with the water and because embedded moving parts are operating within them, such as the power generating turbines, the grids of the forced conduits and the floodgates of the reservoirs, among others [1].

AAR involves the generation of by-products in the cementitious paste from chemical reactions between certain mineral

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constituents of the aggregates used in Portland cement concrete (reactive silica) and the hydroxides dissolved in the solutions of the pores of the latter. However, to cause deleterious effects, the following must exist in the final product or concrete structure: a sufficiently alkaline solution; a critical quantity of reactive silica; ideal temperature conditions; and an equivalent supply of water [3]. Numerous methods have been adopted worldwide for the characterization, quantification, repair and remediation of AAR over time [9–13]. The more disorganized and unstable the microstructure of the minerals in the aggregate, the more reactive it becomes. In decreasing order, these microstructures are the amorphous phase (opal and glass), the microcrystalline phase (chalcedony), the metastable phase (tridimite and cristobalite) and the deformed or altered minerals (deformed quartz and feldspar and altered phyllosilicates). In this reaction, every type of mineral behaves differently due to the mineralogical and microstructural variations of each rock. The product of a reaction is an amorphous silicate with gel characteristics, whose expansion can cause cracks in the matrix and in the aggregate, leading to deterioration of the concrete structure [1,14–17].

AAR manifests as an initial volumetric expansion, a cracking pattern (map-cracking), and a consequent displacement of the structural elements, accompanied by the breakdown of fragments from the surface of the concrete [4,14,18–19]. Due to the potential risks of this type of reaction in civil projects and the impossibility of efficient methods to solve this problem after installation, the best technical/economic solution is prevention [20]. According to Nixon and Sims [3], four indices of concern can be considered regarding the deleterious effects and their combinations, from a P1 classification, in which special actions are not necessary, to P4, where extraordinary measures must be taken. In the case in question, combined factors involving at least 2 of the following methods must be applied: i) restriction of the concentration of alkalis in the porous solution; ii) use of a combination of non-reactive aggregates; iii) reduction of water access; and iv) modification of the gel to obtain a non-expanding chemical relationship.

As noted by Hasparyk [16], one must use cements with low concentrations of alkalis, employ inert aggregates or avoid the diffusion of moisture into the structure. These measures increase costs and decrease efficiency in large, exposed projects. Additionally, active additives, such as pozzolans, fly ash, active silica and rice husk ash, may be used for the mitigation of AAR, in proportions on the order of 10% by mass on average [18,21–23].

In addition to mineral additives, the efficiency of lithium-based compounds to mitigate AAR has been proven. Lithium is used both as a chemical additive in dosing concrete and in the repair of affected structures. Various mechanisms have been proposed to describe their effects on the reduction of expansions associated with AAR [24–26].

Coatings and sealants (silanes, among others) have been used to mitigate AAR, as well as other expansion reactions, due to their hydrophobicity, reducing the relative internal moisture of concrete structures [27].

The use of compounds on the nano scale has been shown to aid in the treatment of susceptible Portland cement concrete structures or those in the early phases of degradation [28]. Additions on the order of 10% by mass of nanostructured silicon dioxide to cement are associated with greater microstructural adhesion of the material and the promotion of pozzolanic reactions between the internal constituents, resulting in increases of up to 26% in the compressive strength (at 28 days), improvement of the workability of the paste, decreases in permeability, and accelerated hydration of the main constituents, in addition to controlling the processes of calcium leaching [29]. Nano-TiO_2 has been adopted for surface modifications, with the objective of developing self-cleaning structures or structures capable of photo-catalysing pollutant gases present in the atmosphere, which is environmentally beneficial [30]. Studies have related the application of this material on the nano scale to acceleration of the hydration of Portland cement, even in the initial curing phase. The study of nano-Fe_3O_4 by Bragança et al. [31], revealed an improvement in the electrochemical stability of Portland cement concretes subjected to artificial environments containing chloride and sulphate ions, with the additional results of filling pores and possibly blocking the growth of gypsum crystals on the aged surface.

1.1. Diagnosis of AAR

In large-scale projects, such as hydroelectric dams, AAR diagnosis begins with visual inspection of the surface of the structure followed by analysis of data from the instruments like tri-orthogonal meters and extensometers and measures of deformations and structural displacements, based on geodesic marks and the high-precision measurement of relative distance [18]. In the laboratory, the diagnosis is obtained from the petrographic analysis of the aggregate or using an optical microscope, followed by standardized tests [9,10,12,23], in specific doses with standard cements and the aggregates, as well as the investigation of chemical alterations through micrographic analysis of the fracture surface by spectroscopy and X-ray diffraction analysis of the elemental chemical component and of the chemical phases present in the specimens. This information is normally extracted from samples from the work, which are characterized, in addition to their mechanical and physical properties, by scanning electron microscopy, X-ray microprobe, X-ray fluorescence, Fourier transform infrared spectroscopy, among other methods [16].

In this study, the microstructural investigation of mineral phases and the crystallographic orientations of the mineral constituents of potentially reactive basalt rocks were carried out with the development and application of electron back-scatter diffraction (EBSD) in a field emission gun scanning electron microscope (FEG-SEM) with a chemical analysis system using an analytical X-ray microprobe (EDS). The advantage of this technique involves simultaneously integrating data from the crystallographic orientations of the aggregate and obtaining the elemental chemical composition of its constituents and their microstructural aspects. Additionally, the integrated use of this information enables the identification of the phases, with their modal distributions, size and shape. According to Morales, Hinrichs and Fernandes [32], another advantage of this technique involves its application to the study of ductile deformed rocks or rocks at the ductile/stress rupture limit. Before this technology, this type of information was only obtained by an optical microscope using universal platinum. This technique has been dismissed as being labour-intensive but is still recommended for determining the orientations of the grain boundaries.

1.2. Pulsed DC plasma

It is estimated that more than 90% of the universe consists of plasma. Plasma is present in natural phenomena such as lightning, the aurora borealis, and stars as well as artificial phenomena such as fluorescent lamps, televisions, and combustion motors, among others. Plasma is considered the fourth state of matter. It is a collection of free particles, normally produced from noble gases (argon and helium), which, when subjected to a specific voltage potential, are converted to an ionized state. The gases, from a macroscopic perspective, are electrically neutral; however, when ionized, they cease to be a gas, and their electrons begin to interact by collisions and electromagnetic radiations, making them conductors. The ionization process occurs when their molecules are subjected to high-energy radiation [33]. The degree of ionization