Evaluation of chloride transport in blended cement mortars containing coal mining waste

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HIGHLIGHTS

- Mortars prepared with activated coal mining waste show lower compressive strength.
- Chloride diffusion is reduced in blended mortars containing activated coal waste.
- Addition of CMW to cement promotes chloride binding in the form of Friedel's salt.
- Microstructure in CMW blended cements becomes more refined as the CMW content increases.

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ABSTRACT

In this study, the effect of the addition of a thermally activated coal mining waste (CMW) on the chloride permeability of blended cements in amounts from 10 to 50% was assessed by salt ponding test. The parameters involved in the infiltration of chloride have been evaluated by XRD, TG and MIP techniques, as well as by electric resistivity measurements. A remarkable improvement in chloride diffusion was found as the CMW content increased, which has resulted in a decrease of one order of magnitude in the chloride diffusion coefficients of specimens containing 50% of CMW ($2.7 \cdot 10^{-12}$ m²/s) with respect to OPC samples ($20 \cdot 10^{-12}$ m²/s). The chemical analyses have shown that immobilization of chloride ions as Friedel's salt takes place as a result of their reaction with the abundant hydrated aluminate phases formed as a consequence of the high alumina content in CMW. Moreover, it has been observed a refinement of the capillary network with the addition of CMW that has been manifested through a decrease in pore size and a subsequent increase in electrical resistivity.

1. Introduction

Concrete is usually regarded as a highly durable material. Nevertheless, most applications of concrete require the use of embedded steel reinforcing bars and this can generate a weakness in the system since steel is known for its susceptibility to deterioration in environments containing water and oxygen (both present in the pore network of concrete). Fortunately, in strong alkaline solutions such as those found in concrete pores, a passivating thin layer of iron oxide is formed around the steel bar, preventing it from being corroded. However, under certain circumstances, the integrity of this protective layer can be compromised, leading to corrosion of the steel and the subsequent cracking and spalling of the concrete, due to the expansion of the corroding bar. One of the major causes of destruction of the passivating film is the introduction of chloride salts in the concrete [1,2].

Corrosion problems in modern concrete caused by chloride ions arise primarily from exposure to aggressive environments, especially those in which concrete is in contact with seawater or de-icing salts [3]. In these cases, additional measures should be taken in order to improve the chloride resistance of the material. The use of Supplementary Cementitious Materials (SCM) is often the preferred course of action.

The reason behind the effectiveness of many SCMs in the enhancement of chloride resistance is due to two factors. Firstly, the addition of pozzolans to cement implies a modification in the microstructure of the hydrated material as a result of the pozzolanic reaction, which usually leads to a more refined pore network. Consequently, the permeability of the system is reduced

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and the introduction of external damaging agents into the material is minimized. On the other hand, chloride ions can be retained by cement hydration products, thus reducing the degree of free chloride infiltration in the specimens. This process is known as chloride binding and it can occur through two different mechanisms: i) physical binding by adsorption on the diffuse layer of C-S-H gels and ii) chemical binding due to the formation of compounds such as Friedel's salt ($Ca_4Al_2O_6Cl_2 \cdot 10H_2O$) or Kuzel's salt ($Ca_4Al_2O_8ClS_{0.5} \cdot 11H_2O$) as a result of the reaction of chloride ions with hydrated calcium aluminate phases [4–6]. It is still unclear which process is more relevant to the reduction of the ingress of chloride ions into cement-based materials, and diametrically opposed positions can even be found in the literature [7–9]. Nevertheless, the addition of supplementary cementitious materials with significant amounts of alumina content leads to an increase in the proportion of aluminate phases and thus, in this scenario, the impact of the formation of Friedel's salt on the chloride profiles may prevail over physical adsorption on C-S-H gels [8,10].

The phases susceptible of giving rise to Friedel's salt formation are the so-called AFm phases. The structure of AFm phases is based on that of the portlandite ($Ca(OH)_2$), consisting on layers of octahedral $Ca(OH)_6$ in which calcium ions have been partially replaced by trivalent cations like Al^{3+} or Fe^{3+}. As a result, anions such as hydroxide, sulfate and carbonate enter the interlayer space to compensate for the excess of positive charge [11]. In the presence of chloride, those anions can be replaced by Cl^-, resulting in the formation of a different AFm phase: the Friedel's salt [12]. Consequently, measures promoting the formation of AFm phases tend to have a positive effect on chloride binding.

Several pozzolans have been successfully employed for the purpose of increasing chloride resistance in cement matrices [5,6,13]. Nonetheless, the massive increase in demand for cement has prompted the need for searching new SCMs. This circumstance, combined with the fact that the development of circular economy guidelines is currently being encouraged, has led to an increased interest in using recycled wastes in the cement industry. In this context, activated coal mining wastes have been presented in previous works as an alternative metakaolinite-based pozzolan, showing promising results with regard to its pozzolanic activity [14–16]. In addition, blended cements prepared with this material present suitable physical and mechanical properties [17–19].

Even though activated coal mining waste blended cements have shown interesting properties, there still exists a knowledge gap in terms of the durability of this type of material. As seen previously, chloride ions are among the primary causes of reinforced concrete deterioration and hence, the performance of this new type of blended cements under such conditions is of great importance. Therefore, the aim of the present work is to analyze the behavior of activated coal mining waste blended cements in the presence of chloride ions. In pursuing this goal, salt ponding test has been performed on mortar specimens prepared with blended cements containing different amounts of activated coal waste and hence, the parameters that govern the diffusion of those ions have been determined. In addition, in order to gain understanding of the process, a chemical study focused on the formation of Friedel's salt has been conducted as well as an assessment of the microstructure of the specimens by means of resistivity and porosimetry measurements.

2. Materials and methods

2.1. Materials

The coal mining waste used in this work was collected from a Spanish opencast mine located in the province on Leon, belonging to the Sociedad Anónima Hullera Vasco-Leonesa. The chemical composition of the raw coal mining waste (RCMW) is compiled in Table 1. Additionally, the mineralogical composition of the material was previously analyzed by X-ray diffraction, being subsequently quantified by the Rietveld methodology. Accordingly, the following crystalline phases have been identified in the raw coal mining waste: quartz (37%), mica (25%), calcite (17%), kaolinite (15%), dolomite (5%) and feldspar (2%) [15,20]. The coal waste was ground until a particle size below 90 µm was achieved and thermally treated at 600 °C for two hours in order to transform the industrial waste into a supplementary cementitious material [21]. The chemical composition of the resulting activated coal mining waste (CMW) is reported in Table 1. It must be noted that CMW exhibits an alumina-silicate nature. More specifically, the main oxides content ($SiO_2 + Al_2O_2 + Fe_2O_3$) amounts to over 86%, which far exceeds the threshold value of 70% set by ASTM-C 618 2017 standard for calcined natural pozzolans [22].

Blended cements were prepared by partial substitution of a commercial Ordinary Portland Cement (OPC) type CEM I 52.5 R provided by Italcementi Group. The chemical composition of OPC is also included in Table 1. With respect to the mineralogy, quantitative XRD analysis has been performed on OPC, obtaining the following results: C_3S (47.4%), C_2S (31.7%), C_3A (9.4%), C_4AF (10.0%) and calcite (1.5%).

Blended cements were prepared by partial substitution of OPC with CMW at amounts of 10% (CMW-10), 20% (CMW-20) and 50% (CMW-50) by weight of binder. A high-speed powder mixer was employed in order to guarantee homogeneity.

In addition, in order to obtain comparable normal consistency between the different formulations, water-reducing admixture Sikament FF was employed in the case of blended specimens.

2.2. Methods

2.2.1. Specimen preparation

Mortar specimens were prepared at a water/binder ratio of 0.5 and a ratio of cementitious material to sand of 1:3, according to the existing EN 196-1 standard [23]. The preparation of CMW-10, CMW-20 and CMW-50 specimens required the addition of 0.4, 0.9 and 1.3% by weight of binder of water-reducing admixture, respectively, in order to obtain similar consistency with respect to OPC mortars.

Three prismatic specimens (4 × 4 × 16 cm) were cast per formulation in order to assess their mechanical properties. The prisms were cured for 28 days by immersion in drinking water and their compression strength was subsequently evaluated as established by EN 196-1. Afterwards, the obtained results were analyzed using the IBM SPSS Statistics software (version 22).

The evaluation of chloride resistance required the preparation of two cylindrical specimens (7.5 × 15 cm) of each type of formu-

Table 1
Chemical composition (wt%) of starting materials.

Oxides	OPC	RCMW	CMW
SiO_2	20.80	49.79	56.63
Al_2O_3	5.70	21.77	25.29
Fe_2O_3	2.89	4.07	4.64
MnO	0.03	0.08	0.08
MgO	1.89	0.64	0.77
CaO	58.99	3.84	4.20
Na_2O	0.93	0.13	0.17
SO_3	4.11	0.27	0.27
K_2O	1.36	2.74	3.09
TiO_2	0.15	1.07	1.17
P_2O_5	0.26	0.13	0.14
LOI	2.79	15.18	3.09