



# The deterioration and environmental impact of binary cements containing thermally activated coal mining waste due to calcium leaching

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## ABSTRACT

Calcium-leaching processes can potentially degrade the structure of a concrete matrix. This problem is studied here through the progressive dissolution of  $\text{Ca}^{2+}$  in both ordinary Portland cement pastes (C-0) and binary cement blends (C-20) containing 20% thermally Activated Coal Mining Waste (ACMW).<sup>1</sup> A series of accelerated tests are conducted that involve the immersion of these cement pastes in a 6M ammonium nitrate solution at a temperature of 20 °C for 7 and for 21 days. A rise in paste porosity was observed, due to increased capillary pore sizes of between 5 and 0.1  $\mu\text{m}$ . In the case of the 20% ACMW pastes (C-20), calcium leaching decreased, probably as a consequence of the pozzolanic effect of the ACMW, while potassium and magnesium leaching increased, due to the presence of the phyllosilicates in the ACMW. The paste compounds most affected by leaching were  $\text{Ca}(\text{OH})_2$ ,  $\text{C}_6\text{AS}_3\text{H}_{32}$ , and  $\text{C}_4\text{ACH}_{12}$ . In general terms, it can be concluded that the incorporation of ACMW into binary cements slightly reduces the calcium leaching phenomena. Concerning the environmental impact assessment, the substitution of 20% OPC by ACMW reduced  $\text{CO}_2$  emissions by as much as 12% and improved energy efficiency by using approximately 19% fewer fossil resources.

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## 1. Introduction

One of the problems of Portland cement concrete is its poor durability in the presence of certain aggressive agents, among which those with a high calcium oxide content. The cement matrix will deteriorate in the presence of pure water and in any other environment that produces calcium lixiviation. This phenomenon is attributed to the dissolution of calcium ions (principally from calcium hydroxides and ions from CSH gels). The decalcification of concrete elements and structures that remain in contact with pure or acidic waters over long periods of time can be affected, as in the case of water pipes and cisterns, dams, and even nuclear waste storage facilities. As the lixiviation of calcium oxide progresses, the cement matrix shows increasing porosity that leads to a loss of its

mechanical strength and functionality.

The hardened cement paste consists of Portlandite, calcium aluminate hydrates and unhydrated clinker embedded in calcium silicate hydrate gel (C–S–H) (Taylor, 1997). This heterogeneous structure induces porosity within the cement paste where dissolved calcium minerals are deposited. Consequently, the exposure of the cement matrix to any aggressive environment with a pH lower than 12.5, such as 6M ammonium solution, leads to its progressive dissolution, due to the migration of the calcium ions from the matrix to the solution (Gaitero et al., 2008). This degradation mechanism of the cement matrix is known as calcium leaching.

According to Goñi et al. (2013), the calcium leaching of cement pastes depends on different factors: the solubility of the hydrated compounds, the type of cement, the Ca/Si ratio, the nature of the pozzolan, and, finally, the pozzolanic rate. According to other researchers, it is also related to the presence of dissolved organic matter, pH, and redox reactivity (Medina et al., 2014; Mulugeta et al., 2011). The degradation of the hydrated compounds of the cement matrix is related to the Ca/Si ratio in the pore solution.

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<sup>1</sup> ACMW, activated coal-mining waste.

Portlandite degradation starts when the calcium concentration in the pore solution is lower than  $20 \text{ mol/m}^3$ , with equilibrium values for the C–S–H gel ranging between 2 and  $20 \text{ mol/m}^3$  (Bernier, 1988). The C–S–H gels dissolve to yield a progressive homogenization of the paste with a lower Ca/Si ratio, while the Portlandite is completely broken down to  $\text{Ca}^{2+}$  and  $\text{OH}^-$ , leaving a network of pores in its place. Porosity and permeability increase, lowering the mechanical strength of the cement matrix (Gaitero et al., 2008). The positive advantages of incorporating pozzolanic material in Portland cement that can resolve and reduce the aforementioned effects are well known (Taylor, 1997; Juenger and Siddique, 2015; Nakanishi et al., 2016). The composition and Ca/Si ratio of the C–S–H gels that form in those blended cements differ from those found in plain OPC (Sáez del Bosque et al., 2014).

Among other materials such as slag (Santamaría et al., 2016) and GGBS, metakaolin, is well known as a supplementary cementitious material that reduces the environmental impact of the Portland clinker manufacturing process and increases the mechanical performance of cement materials and their durability. Over the past few years, industry has been demanding alternative sources for MK, given the ever-greater constraints on the exploitation of natural kaolinite quarries. A cleaner technology for the production of MK involves with the controlled thermal activation of deinking paper sludge and carbon mining waste. An abundance of research and investigation has already demonstrated that the controlled calcination of those waste streams can manufacture a highly reactive MK-containing pozzolanic material, within a temperature range of between 600 and  $750^\circ\text{C}$ . Recent research works have mainly focused on Activated Carbon Mining Waste (ACMW) in substitution of OPC (Frías et al., 2016; Rashad, 2013). Despite scientific progress, there is still an important gap with regard to the behavior of these new matrices in relation to lixiviation processes.

Hence, the main purpose of this paper is to study the influence of this pozzolanic addition on the decalcification process of both a binary cement paste (C-20) and a plain OPC paste (C-0), by examining the leaching behavior of the calcium ions. Excessively lengthy time periods are needed to obtain uniformly leached specimens when studying the impact of calcium leaching on cementitious materials. Calcium leaching in deionized water, the most common aggressive solution in industrial applications, is dependent on diffusion. The leaching rate is therefore extremely slow, at roughly  $30 \mu\text{m}/\text{year}$ . Some accelerated method is therefore needed to reach a certain stage of degradation that is comparable to the long-term damage of natural leaching. Unlike other aggressive environments (freeze/thaw, sulfate attack, and chloride penetration) for concrete, calcium leaching is not standardized and its study is based on previous research works. Two different accelerated methods were found in the literature. The first one consists of applying a strong electrical field to the sample (Saito et al., 1992; Gerard, 1997). As a consequence, a migration of Ca ions of the pore solution towards the cathode occurs, which induces a calcium deficit in the solution and the dissolution of cement hydrates. This method is not driven by diffusion, so the nature of accelerated leaching differs from real conditions. In addition, this method leads to an inhomogeneous decalcification of the cementitious paste, as a function of the distance between the anode and cathode, as well as the strength of the electrical field. The second and the most popular accelerated method, recently (2014–2017) published in previous studies (Gaitero et al., 2008; Phung, 2015), consists of replacing the deionized water with an ammonium nitrate solution. The higher solubility of calcium in this solution leads to faster degradation, when compared with other methods under diffusive-transport conditions, with the same end-products. Although contact between concrete structures and ammonium nitrate does not represent real operative conditions, a 6M ammonium nitrate solution

was used in the present work that accelerates the Ca-leaching degradation kinetics, as explained earlier.

## 2. Materials and methods

### 2.1. Materials

The Coal Mining Waste (CMW) was supplied by the Spanish Coal Group, Sociedad Anónima Hullera Vasco-Leonesa, located in the province of León. ACMW was produced in the laboratory by heating the CMW at  $600^\circ\text{C}$  for 2 h, as described in previous research works (Frías et al., 2011, 2012). The OPC (CEM I 52.5 N) was provided by Financiera y Minera (Italcementi Group). The physical properties and chemical composition of both the CEM I and the ACMW are given in Table 1. The chemical composition was determined by X-ray fluorescence (XRF) using a Philips PW 1404 and an Sc-Mo X-ray tube, while both fineness and particle size distribution were determined by means of laser diffraction (LRD), using a Sympatec Helos 12 KA spectrometer and isopropyl alcohol as a non-reactive liquid (Frías et al., 1991).

The mineralogy of ACMW mainly consists of quartz, mica, hematite, and calcite, while the kaolinite is completely transformed into metakaolin. Further details on mineralogical changes were presented in a previous work (Frías et al., 2011). The cement has the standard Bogue composition of type I Portland cement with 45 wt%  $\text{C}_3\text{S}$ , 24 wt%  $\text{C}_2\text{S}$ , 10 wt%  $\text{C}_3\text{A}$ , and 10 wt%  $\text{C}_4\text{AF}$ , in accordance with the Bogue equation to determine the chemical composition of cement.

Binary cement blends (C-20) were prepared by partially replacing OPC (CEM I 52.5 N) with thermally activated CMW (at lab scale) at  $600^\circ\text{C}$  for 2 h (ACMW), according to previous works (Frías et al., 2011, 2012). Binary blends were prepared by replacing 20% of the OPC with ACMW at a water/binder ratio (w/b) of 0.5. An OPC mix, without ACMW, was also prepared for comparison (C-0).

### 2.2. Methods

#### 2.2.1. Leaching test

In accordance with the experimental methodology reported in previous studies (Gaitero et al., 2008; more recently, Phung, 2015), prismatic cement paste samples of  $1 \times 1 \times 6 \text{ cm}^3$  were cast, according to the EN 196-1 standard (UNE EN 196–1). The samples were cured for 24 h in a chamber at  $20^\circ\text{C}$  and 100% relative humidity. They were then demolded and submerged in a saturated lime solution, to avoid calcium loss over the remaining 27 days of curing. Subsequently, they were immersed in 6M ammonium nitrate solution (Saito et al., 1992) that increases the imbalance and

**Table 1**  
Physical properties and chemical composition of the CEM I 52.5 N and ACMW.

	CEM I 52.5 N	ACMW
100% particles below ( $\mu\text{m}$ )	73	73
90% particles below ( $\mu\text{m}$ )	35.71	33.32
50% particles below ( $\mu\text{m}$ )	12.47	8.33
$\text{SiO}_2$	21.22	58.33
$\text{Al}_2\text{O}_3$	6.39	26.09
$\text{Fe}_2\text{O}_3$	3.19	4.64
$\text{K}_2\text{O}$	1.67	3.09
$\text{CaO}$	61.38	2.16
$\text{TiO}_2$	0.17	1.17
$\text{MgO}$	1.97	0.77
$\text{SO}_3$	0.42	0.27
$\text{Na}_2\text{O}$	0.87	0.17
$\text{P}_2\text{O}_5$	0.20	0.14
$\text{MnO}$	0.04	0.08
LOI	2.49	3.09

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