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Microstructural and durability effects in mortars after 1500 hardening days regarding the addition of volcanic powder of the Calbuco volcano (Chile) as clinker replacement †

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Abstract: Nowadays, the cement industry still constitutes an important pollutant industrial sector. Then, the strategies to reduce its environmental impact are a popular topic of research. One of these strategies consists of partially replacing clinker with other materials. Here, it has been analyzed the effects at 1500 hardening days of the addition of volcanic powder on the microstructure and durability properties of mortars that incorporate 10% and 20% of this addition as clinker replacement. Reference mortars prepared with ordinary Portland cement without additions were also studied. The volcanic powder has been obtained from the last eruption of the Calbuco volcano, placed in the southern Andes between the cities of Ensenada and Puerto Montt (Chile). The mortars were kept in an optimum condition (20ºC and 100% relative humidity) until the testing age. Their microstructure has been characterized using mercury intrusion porosimetry and impedance spectroscopy. As durability parameters, the steady-state chloride diffusion coefficient and the absorption after immersion were determined. According to the results obtained, mortars with volcanic powder showed similar porosities and more refined microstructure compared to reference mortars. Furthermore, the durability properties at 1500 hardening days of mortars which incorporate volcanic powder were adequate, especially regarding the resistance against chloride ingress.

Keywords: sustainability; volcanic powder; very long term effects; microstructure; durability.

1. Introduction

Today, the cement industry still constitutes an important pollutant industrial sector. Therefore, the strategies to reduce its environmental impact are a popular topic of research. One of these strategies consists of replacing partially clinker with other supplementary cementitious materials [1,2], such as additions. Recently, several researches [3,4] have revealed that volcanic powder could have a good performance as addition for cement-based materials. However, these studies have analyzed the effect of volcanic powder at relatively short hardening ages, and the required service life of materials used for building real structures is much longer.

Then, the main purpose of this work is to study the effects in the very long-term (1500 hardening days) of the addition of volcanic powder on the microstructure and durability properties of mortars that incorporate 10% and 20% of volcanic powder as clinker replacement.

2. Materials and Methods

2.1. Materials and sample preparation

The volcanic powder (VP) used in this research came from the last eruption of the Calbuco volcano (41 ° 20 ′ S, 72 ° 37 ′ W, 2003 m.a.s.l.). It is located in the southern Andes, between the cities of Ensenada and Puerto Montt in Chile. Its last subplinian eruption occurred on April 22-23, 2015, Analyses of the erupted debris reveal the presence of porphyritic basaltic andesite (~ 55% by weight of SiO_2) [5]. The particle size distributions of the debris revealed particle fractions from 3 μm to 350 μm,[6]. In this study, the volcanic powder was sifted and the VP particles used as an addition were less than 75 μm. The chemical analysis of the VP revealed that its main components are silica, aluminum and iron.

Three kinds of mortars are studied in this research. First of all, a reference mortar made only with ordinary Portland cement CEM I 42.5 R (Spanish and European standard UNE-EN 197-1 [7]), designed as REF in the results and discussion section. Regarding the specimens with VP addition, two different types of mortars were prepared, which incorporated a 10% and 20% as a replacement of the abovementioned cement CEM I 42.5 R. These mortars were respectively named as VP10 and VP20. The water to cement ratio was 0.5 and the aggregate to cement ratio was 3:1 for all the studied mortars. The fine aggregates accomplished the prescriptions of standard UNE-EN 196-1 [8].

Cylindrical specimens with 10 cm in diameter and 15 cm high were prepared. They were stored in a chamber at 20°C and 95% relative humidity (RH) during the first 24 hours. After that, they were de-molded and cut for obtaining disks with 1 cm thickness.Finally, these samples were kept in an optimum laboratory condition (20°C and 100% RH) up to the testing age (1500 hardening days).

2.2. Experimental techniques

The microstructure of the mortars was characterized using mercury intrusion porosimetry and impedance spectroscopy.

In relation to mercury intrusion porosimetry, the porosimeter used was a Poremaster-60 GT model manufactured by Quantachrome Instruments (Boynton Beach, Florida, USA). Before the test, the specimens were dried in an oven at 50°C for 48 hours. The results analyzed in this work were total porosity, pore size distribution and percentage of Hg retained at the end of the experiment. Two measurements were made on each type of mortar.

Regarding the impedance spectroscopy, it allows to get global information of the pore structure of the samples [9,10]. In this work, the measurements were performed using an Agilent 4294A analyzer (Agilent Technologies, Kobe, Japan). This device takes capacitance measurements ranging between 10^{-14} F and 0.1 F, with a maximum resolution of 10^{-15} F. Circular electrodes with 8 cm diameter were used, consisting of flexible graphite attached to a piece of copper with the same diameter to obtain the impedance spectra. The frequencies ranged between 100 Hz and 100 MHz. Contacting and non-contacting methods were used [9]. The experimental data were fit to the equivalent circuits proposed by Cabeza et al. [36]. Those circuits consisted of several resistances and capacitances [10]. The R_1 resistance provides data about the percolating poresin the sample, the R_2 resistance provides information about the pores in general, the C_1 capacitance provides information about the solid fraction of the sample, and the C_2 capacitance is associated with the surface of the pores in contact with the electrolyte that fills the pore network of the material [10]. Here, due to their greater accuracy, only the values of the parameters R_2, C_1 and C_2 with the non-contacting method are analyzed. The value of the R_1 resistance, which can be only obtained using the contacting method, was used for obtaining the steady-state chloride diffusion coefficient. Eight different disks were analyzed with this technique for each mortar type.

The durability-related parameters analyzed in this research have been the absorption after immersion and the steady-state chloride diffusion coefficient.

The absorption after immersion was determined according to the ASTM Standard C642-06 [11] and six samples were tested for each kind of mortar studied.

The steady-state chloride diffusion coefficient has been obtained from the electrical resistivity of the saturated sample. The resistivity was calculated from the R_1 impedance spectroscopy values obtained in saturated samples. As has been previously explained, the R_1 impedance resistance is related to the pores that cross the sample [9] and is therefore equivalent to the electrical resistance of the sample [12]. For each binder, six different samples were tested. Finally, the steady-state diffusion coefficient was calculated using the following expression [33]:

$$D_S = \frac{2\times10^{-10}}{\rho} \quad (3)$$

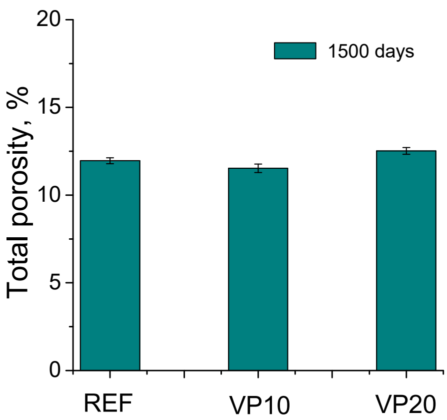
where: D_s is the chloride steady-state diffusion coefficient through the sample (m^2/s) and ρ is the electrical resistivity of the specimen ($\Omega\cdot m$).

3. Results and discussion

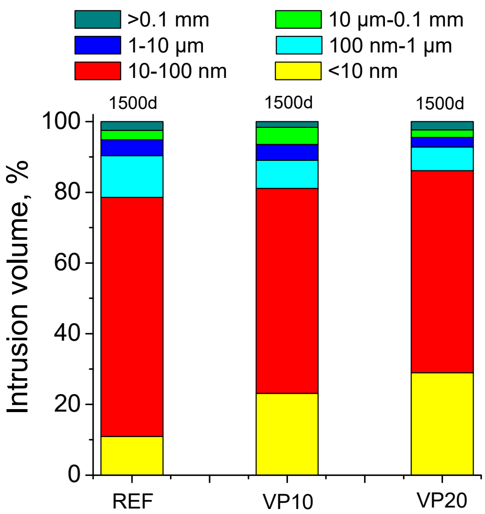
Below were shown the results of total porosity, the pore size distributions and the percentage of mercury retained at the end of the experiment in the mortars after 1500 hardening days. The pore size distribution was analyzed considering the next diameter intervals: <10 nm, 10-100 nm, 100 nm to 1μm, 1-10 μm, 10 μm to 0.1 mm, and >0.1 mm

The results for total porosity are represented in Figure 1.a. The porosity of VP samples increased as the percentage of VP rose. On the one hand, the VP10 mortar showed a very similar porosity to the reference one at 1500 days of hardening. On the other hand, for the VP20 samples, the porosities were scarce higher than those presented by the reference cement.

Regarding the porous structure of the specimens with VP (see Figure 1.b), it was more refined for both the VP10 and VP20 ones than for the reference mortar at 1500 hardening days, as suggested the higher volume of pores with diameters lower than 100 nm, and especially those in the range <10 nm. This fact would be indicative of the beneficial effect in the very long term of VP addition, produced by the formation of new solid phases as products of pozzolanic reactions of volcanic powders, entailing a closer microstructure.



(**a**)

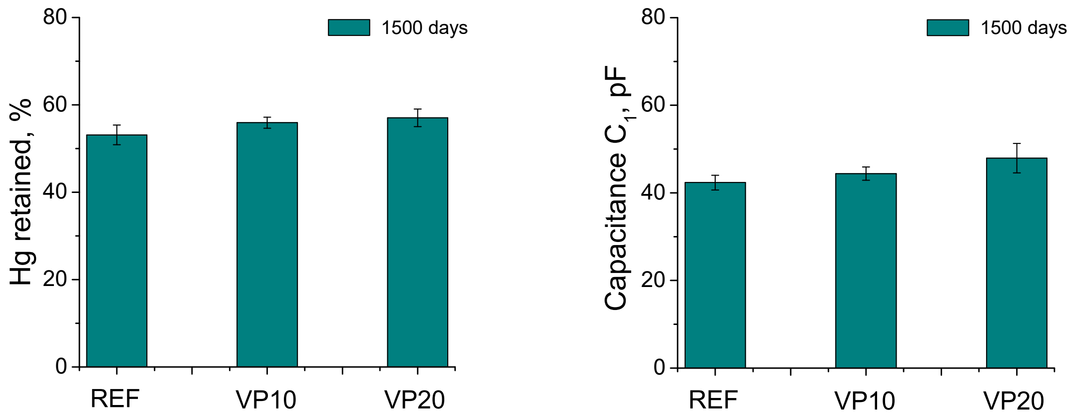


(**b**)

Figure 1. (**a**) Total porosity results of the mortars studied; (**b**) Pore size distributions of the analyzed mortars.

With respect to the percentage of Hg retained in the samples at 1500 hardening days, the Figure 2.a shows that the values of this parameter obtained for VP mortars were greater than those for the reference specimens. The percentage of Hg retained provides information about the tortuosity of the pore network of the material. Therefore, the abovementioned result would suggest that VP specimens had a higher pore network refinement, coinciding with the pore size distribution results previously described and discussed.

In relation to impedance spectroscopy results, in the Figure 2.b it can be observed that the capacitance C_1 values noted for the VP10 and VP20 samples were relatively similar to those noted for reference specimens at 1500 hardening days. This parameter gives data about the solid fraction of the samples [9]. Consequently, the C_1 capacitance should increase when solids are formed as a consequence of the development of clinker hydration and pozzolanic VP reactions. This parameter does not depend on the distribution of the pore diameters. Therefore, the C_1 values at 1500 hardening days would indicate that the solid fraction of VP10, VP20 and reference mortars was similar. In view of that, the results of C_1 agree with the total porosity results obtained for all the mortar types analyzed, since they also show very similar values independently of the binder.



(**a**) (**b**)

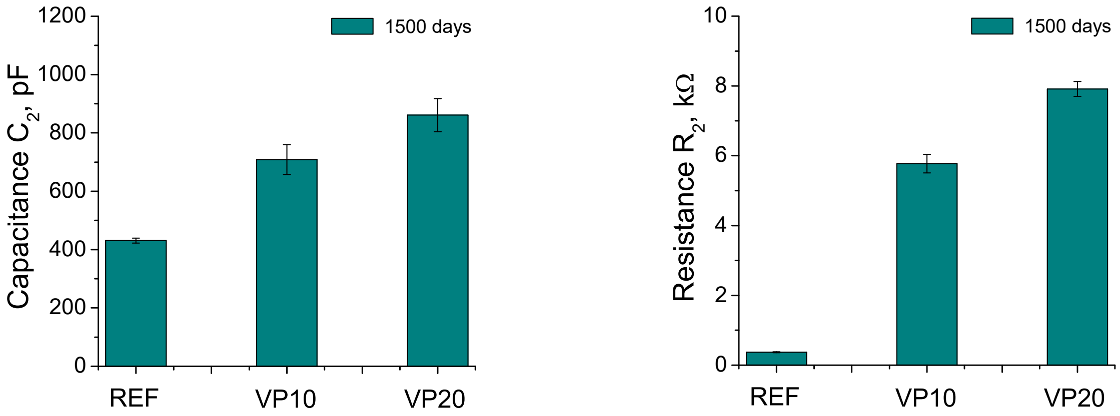
Figure 2. (**a**) Percentage of mercury retained at the end of the mercury intrusion porosimetry test for the binders studied; (**b**) Impedance spectroscopy C_1 capacitance for the mortars studied.

The results of the C_2 capacitance of the different samples analyzed are represented in Figure 3.a. This parameter is related to the surface of the pores that are in contact with the electrolyte retained in the pores network of the material [14]. Therefore, this parameter is linked to the formation of the C-S-H gel layer, which progressively fills the pores. The C-S-H gel is formed on the surface of the pores and would produce rough structures that increase the specific surface of the pore, as well as the tortuosity of the microstructure. This increase in the specific pore surface is linked with an increase in the solid-electrolyte interface, which results in higher values of C_2 capacitance. At 1500 hardening days, the C_2 capacitance values were noticeably higher for the samples VP10 and VP20 in comparison with the reference mortar. These results would be in keeping with the higher pore refinement noted for VP mortars in their pore size distributions by intervals, explained in relation to the effects of pozzolanic reactions of the volcanic powders in the microstructure.

The results of R_2 resistance is depicted in Figure 3.b. This resistance is related to the electrolyte that fills the pores in the specimen [9]. At 1500 hardening days, the R_2 values were higher when greater is the VP content in the sample. This would indicate that the addition of VP increased the relative volume of smaller pores, being also in agreement with porosimetry and capacitance C_2 results already discussed.

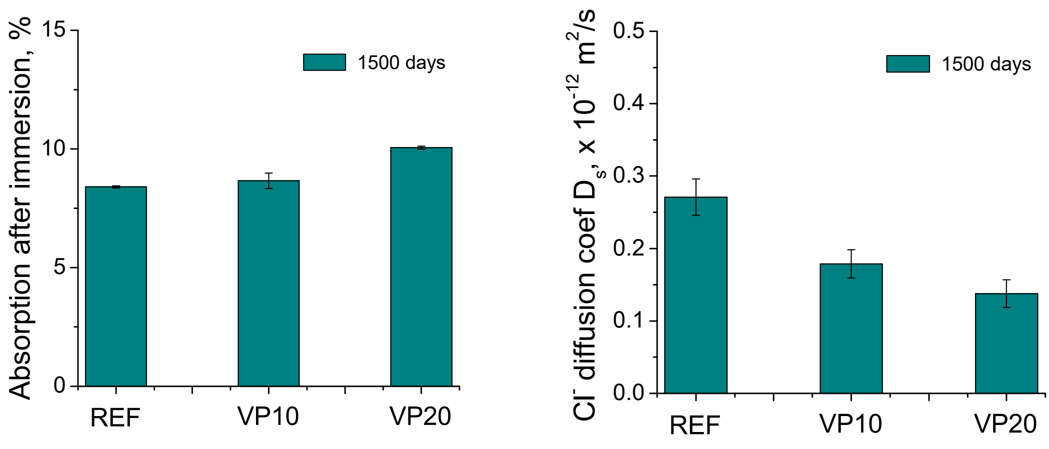
Regarding the absorption after immersion parameter, the measurements for the mortars analyzed are represented in Figure 4.a. The percentage of water absorption at 1500 hardening days was slightly higher in VP20 samples. However, the percentages of absorption in VP10 and reference samples were very similar.

Finally, the results of the steady-state chloride diffusion coefficient obtained from the resistivity of the saturated sample at 1500 hardening days are shown in Figure 4.b. It can be seen that the samples with VP presented lower values than reference mortars, which would indicate a very good performance of this addition regarding chloride ingress resistance. This result could be related to the greater refinement of the microstructure of the VP10 and VP20 mortars with respect to reference ones. The presence of a greater proportion of pores with smaller diameters would make more difficult the migration of aggressive chloride ions through the material, which would lead to lower values of the diffusion coefficient, as has been observed.



(**a**) (**b**)

Figure 3. (**a**) Impedance spectroscopy C_2 capacitance for the mortars studied; (**b**) Impedance spectroscopy R_2 resistance for the mortars studied.



(**a**) (**b**)

Figure 4. (**a**) Results of absorption after immersion parameter for the mortars analyzed; (**b**) Steady-state chloride diffusion coefficients obtained for the different binders studied.

4. Conclusions

The main conclusions to be drawn from the results previously discussed can be summarized as follows:

- At 1500 hardening days, the VP mortars showed a greater refinement of the pore structure in comparison with the reference mortars. This fact would be indicative of the beneficial effect in the very long term of this addition, produced by the formation of new solid phases as products of pozzolanic reactions of volcanic powders
- The results at 1500 days obtained using the non-destructive impedance spectroscopy technique were overall in agreement with the results obtained with mercury intrusion porosimetry.

- The durability properties in the very long term analyzed in this work were overall adequate for VP mortars, highlighting their very good performance regarding chloride ingress resistance.

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Conflicts of Interest: The authors declare no conflict of interest.

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