



# Decoupling the physical and chemical effects of supplementary cementitious materials on strength and permeability: A multi-level approach

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## ABSTRACT

Supplementary cementitious materials (SCMs) represent an alternative for the industry to achieve sustainability by reducing cement contents without significant compromises of the mechanical properties and enhancing durability. SCMs play a dual role during hydration: a physical effect promoting nucleation and cement hydration and a chemical effect through pozzolanic activity. Rice husk ash (RHA) and natural pozzolans (NP) were evaluated using compressive strength and durability tests in a multi-level experimental program. RHA increased the strength more than NP, which is well explained by its prominent chemical effect (78%) assessed by isothermal calorimetry and its high amorphous silica content. Both RHA and NP produced significant reductions in the permeability of the concrete, which is mostly explained by the chemical effect. Decoupling the physical and chemical effects of a SCM allows for optimisation of its manufacturing process.

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## 1. Introduction

The cement industry has faced new environmental challenges in the last decades, such as energy consumption and CO<sub>2</sub> emission reductions [1]. Developments addressing these challenges have focused on the exploration and use of supplementary cementitious materials (SCMs) to reduce the cement content in concrete mixes [2–6] and enhance the durability of the material to increase the service life of concrete structures [7,8].

Rice husk ash (RHA) is obtained from agricultural waste, and has been widely investigated [9–11]. World rice production rose to approximately 722 billion tonnes in 2011 [12]. The main uses of rice husks are as fuel for the paddy milling process [13] and electric power plants [14]. Effects of rice husk ash on concrete strength ([9,10,13,15–17]) and durability ([15,18–21]) are well documented in the literature. RHA reactivity mainly depends on the particle size

distribution ([15,17,22]) and the burning temperature and time of the husks [17,23,24]. The nature of the reaction product of RHA and portlandite (CH) has been reported as secondary C–S–H gel [11,25].

Natural pozzolans (NP) from volcanic origins have been used in Chilean blended cements since the 1960's. While chemical and physical properties vary depending on the pozzolan source, performance in compressive strength and durability have been studied in different places where this material is available [26–29].

The effects of SCMs can be analysed as two simultaneous, non-divisible contributions occurring in a cementitious system:

1. *Chemical contribution*, referred as the pozzolanic effect, which is related to the formation of hydration products from CH produced during cement hydration and the amorphous silica phases present in supplementary cementitious material [3,30]. The rate of reaction depends on the particle size (finer materials have more specific surface to react) and the availability of amorphous silica, water and CH.
2. *Physical contribution*, referred to as the filler effect, is related to changes in the particle spacing and surface availability for nucleation of hydration products [3,31].

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As stated in the literature [3,31], the filler effect can be decomposed into dual opposing physical interactions of the inert material with the cementitious matrix [32]. First, the dilution effect is equivalent to increasing the water-to-cement ratio (w/c). Because inert filler does not produce hydration products, the separation between cement particles increases, which makes hydration products less compact at the same water-to-solids ratio. The second effect, related to the additional surface added by the fine inert material particles, provides more nucleation sites for the hydration products [3] and is referred to as the heterogeneous nucleation effect. Previous studies have shown that these effects may be considered additive [33].

While several studies have characterised the effects of natural pozzolan and rice husk ash on the compressive strength and permeability of concrete separately ([9,17–22,26,27,29,34,35]), there is a lack of investigations comparing both materials under the same testing conditions. In addition, the physical and chemical effects are commonly not distinguished, and the results are reported as the overall performance of the corresponding supplementary cementitious material. Because particle size distribution affects chemical reactivity and physical interaction of the addition material, a thorough characterisation of its performance requires assessing both contributions separately.

This paper assesses RHA and NP performance by focusing on the chemical and physical interactions. In addition, a multi-level (cement paste, mortar and concrete) approach and testing program is presented.

## 2. Materials and methods

To assess the physical (filler) and chemical (pozzolanic) effects of SCMs accurately, two types of materials were used in this study. First, chemically inert filler was used as a reference for the physical interaction of particles on cement hydration and its influence on the measured properties. Secondly, SCMs, containing amorphous silica phases, were evaluated and compared in the same experimental program. Because these materials exhibit both behaviours simultaneously (filler and pozzolanic), inert filler is used to assess the chemical contribution of the SCMs by allowing an estimate of the physical component by itself.

### 2.1. Material manufacture and characterisation

Type I ordinary Portland cement (OPC) conforming to ASTM C150 was used in all tests conducted in this study.

Rice husk ash (RHA) was manufactured from 24 kg of locally obtained rice husks. Husks were burnt under controlled conditions in two steps: in the first step, batches of approximately 6 kg were burned in an industrial furnace at approximately 600 °C for 4 h; in the second step, the ash produced was re-burnt at 700 °C for 3 h in batches of approximately 50 g in small crucibles using a laboratory furnace. The two-step procedure was based on previous research that showed that optimal silica production was achieved by heating rice husks at 700 °C for 6 h [23], which created uniformity in the combustion process and removed any remaining organic matter.

Natural pozzolan (NP) from a volcanic source was obtained from a local blended cement manufacturer. This variety of pozzolans has been used in Chilean cements as SCMs for decades and was considered in this study as a comparative performance reference of a widely used SCM in the local concrete industry.

Inert filler was obtained by crushing mill graded siliceous sand conforming to ASTM C778 in a jar mill using steel balls as the grinding media. This sand was selected instead of commercial concrete filler due to its high quartz content and, therefore, its non-pozzolanic nature [3,31]. Two particle size distributions (PSD) were

obtained: coarse filler by grinding sand for 3 days in the jar mill (FILL3), and fine filler by reprocessing the coarse filler in a smaller jar mill for one week (FILL7). This was done to have comparative PSD boundaries for all the SCMs considered in this study so that physical and chemical interactions could be compared.

RHA and NP were ground prior to grinding in a jar mill for 1 h to achieve a uniform PSD. The chemical composition of the OPC, RHA and NP was measured using XRF and is presented as oxides in Table 1. High amounts of SiO<sub>2</sub> were identified in both SCMs, but it was especially high in the RHA. In addition, the PSD was measured for all the materials used.

Thermogravimetric analysis (TGA/DTG) of the materials was conducted under a nitrogen flux, with a temperature ramp up to 1000 °C. The DTG results are presented in Fig. 1, were no significant decomposition is observed for the inert filler, which is consistent with a mainly quartz composition and suggests a high chemical stability. The weight loss of the RHA at approximately 100 °C is attributed to the loss of water adsorbed on the particles and retained in the particle mesopore structure [36,37]. A clear decarbonation peak is shown on the OPC plot slightly above 700 °C.

### 2.2. X-ray diffraction

Quantitative X-ray diffraction (QXRD) analysis was performed to determine the mineral composition of the RHA and NP. Testing was performed between 10 and 75° 2 $\theta$  at a 0.02° per second sampling rate. Commercially available software (EVA and TOPAS) was employed for phase identification and Rietveld refinement, respectively. Fluorite was selected as the internal standard to account for the amorphous fraction and correct the Rietveld results, based on the procedure proposed by Chancey et al. [38].

### 2.3. Isothermal calorimetry

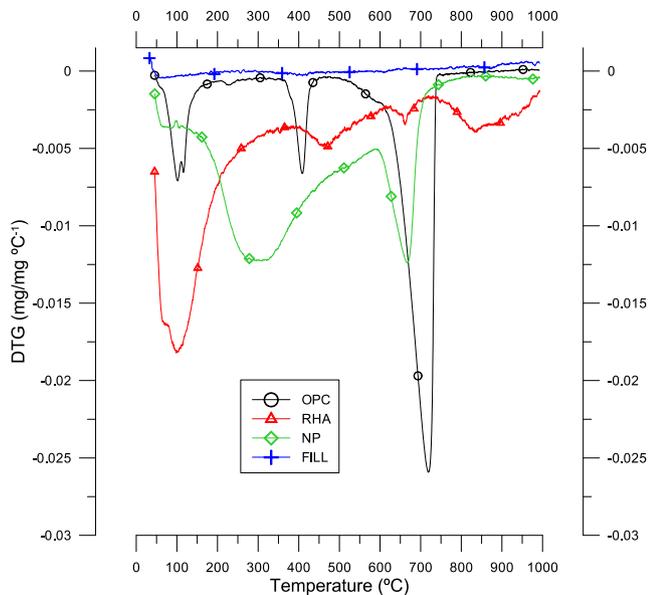
Isothermal calorimetry is a widely used technique to characterise hydration and blended cement systems [39,40]. In this particular study, tests were conducted using a TAM Air Isothermal Calorimeter to assess the impact of different SCMs and inert filler on the hydration kinetics. Cement pastes with water-to-cementitious materials ratio by weight (w/cm) is 0.5 in all cases. The substitution levels of 20% by weight of the OPC by RHA, NP, FILL3 and FILL7 were used. Tests were carried out at 23 °C for 7 days. Duplicate samples were measured for each mixture.

### 2.4. Compressive strength

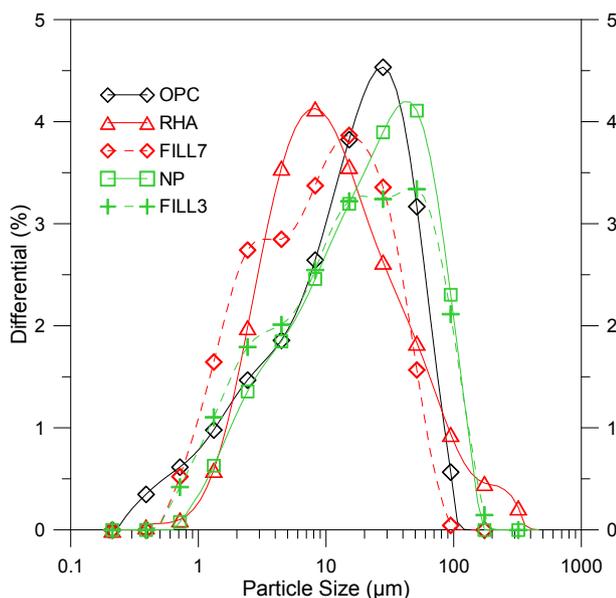
The compressive strength was also measured to evaluate the impact of different SCMs on the mechanical behaviour. This assessment was performed at two different levels: cement paste

**Table 1**  
Chemical composition of the OPC, NP and RHA.

Percentage of oxides (%)	OPC	RHA	NP
SiO <sub>2</sub>	11.3	84.20	66.97
Al <sub>2</sub> O <sub>3</sub>	3.29	0.56	13.51
Fe <sub>2</sub> O <sub>3</sub>	3.33	1.13	1.82
CaO	73.9	1.38	3.33
Na <sub>2</sub> O	0.48	0.38	3.87
K <sub>2</sub> O	0.36	4.30	3.32
MnO	0.18	0.62	0.08
TiO <sub>2</sub>	0.31	0.04	0.24
MgO	<0.01	0.56	0.65
P <sub>2</sub> O <sub>5</sub>	0.10	0.99	0.14
LOI	2.68	5.05	6.06
Specific gravity	3.184	2.158	2.432



**Fig. 1.** Differential thermogravimetric (DTG) curves of the OPC, NP, RHA and inert filler (FILL).



**Fig. 2.** Particle size distributions of the RHA, NP, OPC, coarse and fine inert fillers (i.e., FILL3 and FILL7).

and mortars. Cement pastes were used to evaluate the effects of a broad range of OPC-by-SCMs substitution levels in a pure cementitious matrix environment, while mortar mixtures were used for assessing the interaction between the SCM matrix and aggregates.

#### 2.4.1. Cement paste

Paste mixtures were made using 0, 10, 20, 30, 50 and 75% OPC-by-SCM substitution levels by weight for the four materials studied (RHA, NP, FILL3 and FILL7). Cubic specimens with 2 cm sides were used with a constant w/cm ratio of 0.5 in all cases. Moulds were covered with a plastic sheet to avoid evaporation and kept at  $20 \pm 3$  °C for 1 day. Subsequently, specimens were removed from moulds and stored in sealed bags in a  $20 \pm 3$  °C chamber until the time of testing. Compressive strength tests were conducted at 7, 28

and 90 days with a constant 1800 N/s load rate in all cases.

To compare the observed SCM effects on strength with porosity variations of the cement matrix, 100% OPC pastes were tested in the same conditions with w/cm ratios of 0.4, 0.45, 0.5, 0.55 and 0.6. This allows expressing the SCM's positive/negative impacts on the compressive strength as equivalent quantities of cement addition/subtraction, or as a variation of the w/cm ratio.

#### 2.4.2. Mortar

Mortar mixtures were made with 0, 10, 20 and 30% OPC-by-SCM substitution levels by weight. RHA and NP were used for all cases, while FILL3 substitution was made at the central level of substitution (20%) only to estimate the filler effect on the compressive strength at this level. Cubic specimens with 5 cm sides were made using a constant w/cm ratio of 0.5 in all cases. Additionally, some adjustments were made to keep the cementitious paste (OPC + SCM + mixing water) volume constant in all mixtures, so that the paste-to-aggregate ratio would not change. Standard graded sand conforming to ASTM C778 was used in all mortar mixtures. Specimens were removed from the moulds after one day of curing and stored submerged in tap water inside a  $20 \pm 3$  °C and 95% RH chamber until time of testing. Compressive strength tests were conducted at 3, 7, 28 and 90 days with a constant 1800 N/s load rate in all cases. Mixture designs of the mortar series are detailed in Table 2.

#### 2.5. Durability

The effect of different SCMs on durability was measured using concrete specimens. For this purpose, 0, 10, 20 and 30% OPC-by-SCM substitution levels by weight were considered using RHA and NP. As in the mortar series, FILL3 was used in the central level of substitution. Similarly to the mortars, some adjustments were made to keep the cementitious paste volume (OPC + SCM + mixing water) constant in all mixtures, so that the paste-to-aggregate ratio was constant. Four 10-by-20 cm cylinder specimens were made at each substitution level with a constant 0.5 w/cm ratio. A commercial superplasticiser admixture was used at a weight dosage of 0.8% of cementitious materials to improve workability. Specimens were kept in moulds for one day, and then were cured submerged in tap water in a  $20 \pm 3$  °C and 95% RH chamber until 90 days of age, when all durability tests were performed. Mixture proportions can be found in Table 3.

##### 2.5.1. Chloride ion penetration

The electrical chloride ion penetration test was performed according to the ASTM C1202 standard. Two 51 mm thick slices from two different concrete cylinders were tested for each of the concrete mixtures.

##### 2.5.2. Electrical resistivity

Electrical resistivity was measured using two 10 by 20 cm cylindrical specimens for each mixture based on the axial-measurement method described by Spragg et al. [41] to compare the filler and pozzolanic effects of the SCMs on concrete pore percolation. In this method, two stainless steel plates are placed at the ends of the 10-by-20 cm cylinder and connected to the same surface resistivity meter used in the Wenner probe apparatus [42]. Electrical resistance values are obtained and normalised by the cross sectional area to length ratio of the cylinder to calculate the bulk resistivity of the specimen. Specimens were stored submerged in water during the whole curing period and tested in a saturated condition.

This method was selected because it is completely non-destructive, simple and able to produce immediate results, as

**Table 2**  
Mixture proportions of the mortar specimens.

Level (%)	SCM ID	W/cm	OPC (kg/m <sup>3</sup> )	Mixing water (kg/m <sup>3</sup> )	SCM (kg/m <sup>3</sup> )	Std. Sand (kg/m <sup>3</sup> )
0	0	0.5	504.1	252.0	0	1562.6
10	RHA	0.5	445.5	247.5	49.5	1562.6
	NP	0.5	448.3	249.1	49.8	1562.6
20	RHA	0.5	389.0	243.1	97.2	1562.6
	NP	0.5	393.8	246.2	98.5	1562.6
	FILL3	0.5	397.2	248.3	99.3	1562.6
30	RHA	0.5	334.4	238.9	143.3	1562.6
	NP	0.5	340.7	243.3	146.0	1562.6

**Table 3**  
Mixture proportions of the concrete specimens for durability testing.

Level (%)	SCM ID	W/cm	OPC (kg/m <sup>3</sup> )	Mixing water (kg/m <sup>3</sup> )	SCM (kg/m <sup>3</sup> )	Fine sand (kg/m <sup>3</sup> )	Coarse sand (kg/m <sup>3</sup> )	Coarse Agg. (Kg/m <sup>3</sup> )
0	–	0.5	350.0	175.0	0	185	647	1036
10	RHA	0.5	309.4	171.9	34.4	185	647	1036
	NP	0.5	311.3	173.0	34.6	185	647	1036
20	RHA	0.5	270.1	168.8	67.5	185	647	1036
	NP	0.5	273.5	170.9	68.4	185	647	1036
	FILL3	0.5	275.8	172.4	68.9	185	647	1036
30	RHA	0.5	232.2	165.9	99.5	185	647	1036
	NP	0.5	236.6	169.0	101.4	185	647	1036

well as consistent results throughout subsequent measurements. In addition, Spragg et al. showed that there is a linear correlation between measurements using this method and values obtained using the standard Wenner probe method [41].

### 3. Results and discussion

#### 3.1. Particle size distribution (PSD)

As seen in the figure, FILL3 has a similar PSD to NP while FILL7 is closer to RHA. Both inert fillers represent good approximations of the SCMs physical characteristics from a particle size perspective. FILL3 and FILL7 are good boundaries to the RHA from a PSD perspective, allowing a more accurate measurement of the chemical contribution of this SCM. All the materials have PSDs in a similar range of the particles of the OPC, which allows for comparing these materials with similar conditions of exposed surface.

#### 3.2. X-ray diffraction

Diffraction patterns are presented in Fig. 3 and Table 4. They include the main peaks and crystalline phase composition, along with the amorphous material content.

Rietveld refinement results were achieved with a goodness of fit (GOF) indicator of 1.2 and a Rexp of 3.0, which indicate a good agreement between the experimental data and Rietveld computed pattern and good data quality, respectively.

Both the RHA and NP show a large amount of amorphous phases of approximately 92%, and a relatively small amount of Quartz, approximately 1.5%. When comparing this with the XRF results shown in Table 1, it can be concluded that most of the total SiO<sub>2</sub> phases exists as amorphous forms of silica. Therefore, the RHA, having more amorphous silica, would exhibit a higher chemical activity than the NP. Additionally, the RHA might exhibit higher activity due to the presence of beta C<sub>2</sub>S that can be formed during manufacturing at 700 °C and remain at ambient temperature without a stabiliser if the beta C<sub>2</sub>S crystals are sufficiently small [43]. These two differences suggest that the RHA might yield higher mechanical and physical performance than the NP when used as a

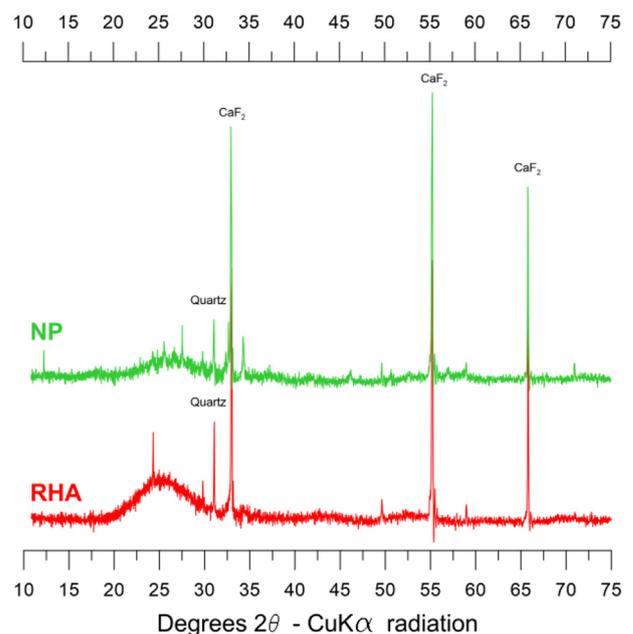


Fig. 3. X-ray diffraction pattern of the RHA and NP used for Rietveld refinement.

SCM in concrete.

#### 3.3. Isothermal calorimetry

The heat flow results show a slight acceleration of the hydration reaction when finer materials are added to the sample. This is attributed to the physical effect of the SCMs on the hydration of the OPC [32,33]. This physical effect can be clearly seen in the total heat plots (Fig. 4a), where even chemically inert materials (FILL3 and FILL7) exhibit a higher heat release in time than the OPC.

Chemical interactions can be observed for the RHA and NP even at this early stage of hydration based on the differences between the inert fillers. Because the PSD of FILL7 is similar to RHA and FILL3 is similar to NP (Fig. 2), the differences in the heat released between

**Table 4**

QXRD analysis of the RHA and NP, including computed amorphous content based on an internal standard correction procedure.

Mineral Name	NP (% by wt.)	RHA (% by wt.)
Quartz	1.2	1.5
Albite	1.3	0.4
Oligoclase	1.7	0.6
Sanidine	0.4	1.4
Fluorite (I.S.)	11.9	11.7
Andesine	0.9	0.4
Anhydrite	0.1	0.3
Actinolite	0.3	0.0
Calcite	2.4	3.1
Beta C <sub>2</sub> S	0.0	0.6
Amorphous	91.8	91.6
		I.S. = Internal standard

these pairs are an estimate of the chemical activity of the pozzolanic material. The RHA heat evolution (Fig. 4a) shows clear differences with FILL7, which suggests a significantly higher chemical reactivity of this material at early ages. This can be attributed to the high silica content in combination with finer PSD, which provide additional specific surface for pozzolanic reaction and enhanced nucleation of OPC. It has been shown previously that there is a strong correlation between heat release, chemically bound water and therefore, degree of hydration of blended systems [39].

On the contrary, for the NP, the chemical reactivity is almost negligible during the first 7 days because FILL3 and NP heat plots are very similar. This may be attributed to the coarser PSD of the NP, which can delay the pozzolanic reaction and only provides a similar physical contribution as FILL3 at 7 days. In addition, NP has a lower silica content compared to RHA (Table 1), which further explain the differences in the observed hydration kinetics.

### 3.4. Compressive strength

#### 3.4.1. Compressive strength for the pastes with w/cm ratios of 0.5

Results of the compressive strength test on paste specimens are shown in Fig. 5 a, b and c for 7, 28 and 90 days of age, respectively. They are expressed as ratios using the w/cm 0.5100% OPC mixture as a reference, which is also represented graphically by a bold horizontal grey line. Porosity variations are represented as horizontal lines and corresponds to the 100% OPC mixes with w/cm variation according to the experimental program. This allows for

comparing the effect of the SCM substitution with changes in the w/cm in a 100% OPC paste. Therefore, the SCM overall reactivity can be expressed as the expected performance of a given OPC added mass.

RHA pastes show very early strength development compared to the other series (Fig. 5a) as exhibited by  $R_{SCM}/R_{OPC}$  ratios of 1.25–1.50 even at high substitution levels. It can be concluded that these results are the effect of physical and chemical interactions of the RHA during hydration, as observed in isothermal calorimetry (Fig. 4).

FILL7 and FILL3 series exhibit very low  $R_{SCM}/R_{OPC}$  ratios ranging between 0.10 and 0.80 meaning the physical interactions are low during the first 7 days. Because FILL7 and FILL3 are boundaries to the RHA from a PSD perspective (Fig. 2), the large differences in the  $R_{SCM}/R_{OPC}$  ratios suggest that a considerable pozzolanic reaction occurs in the RHA series during the first 7 days. The high amount of amorphous material found in the XRD analysis explains this observation. This conclusion agrees with previous findings that RHA can be as reactive as silica fume [16], another SCM with a very high amorphous silica content.

FILL7 shows a higher level of hydration activation than the FILL3 paste, as expected from the calorimetry results. Because the substitution level is the same in both series with inert filler, the activation observed can be attributed to differences in the PSD only; thus, hydration enhancement occurs as extra space is available and the filler surface acts as nucleation sites for clinker phases [3,31].

The NP results reflect negligible pozzolanic activity during the first 7 days showing  $R_{SCM}/R_{OPC}$  ratios below the inert series (FILL7 and FILL3) suggesting a lower acceleration of hydration due to the filler effect. This low chemical activity is also observed in the total heat release of the NP compared to FILL3 and OPC (Fig. 3b), which can be attributed to the coarser PSD of the NP compared to FILL3 and FILL7, as seen in Fig. 2, which delayed the pozzolanic reaction of the amorphous silica phases.

At 28 days age (Fig. 5b), the behaviour of the RHA series still outperforms that of 100% OPC; however, the ongoing hydration of the OPC tends to reduce initial differences. For instance, at 75% substitution level, the specimens exhibit a  $R_{SCM}/R_{OPC}$  ratio below 1.0 and the maximum  $R_{SCM}/R_{OPC}$  ratio decreased from 1.5 at 7 days to 1.25 at 28 days. The NP starts to develop pozzolanic activity, which is clear at substitution levels higher than 50%, where this pozzolanic reactivity becomes noticeable when compared to the series exhibiting only physical interactions (FILL3 and FILL7).

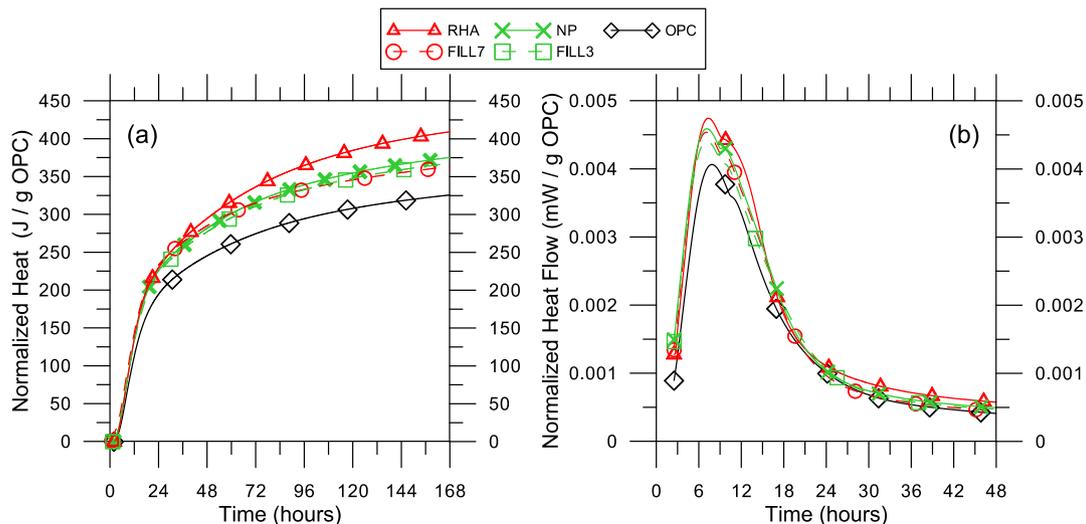


Fig. 4. Total heat (a) and heat flow (b) of w/cm 0.5 pastes containing 20% RHA, NP, FILL3 or FILL7.

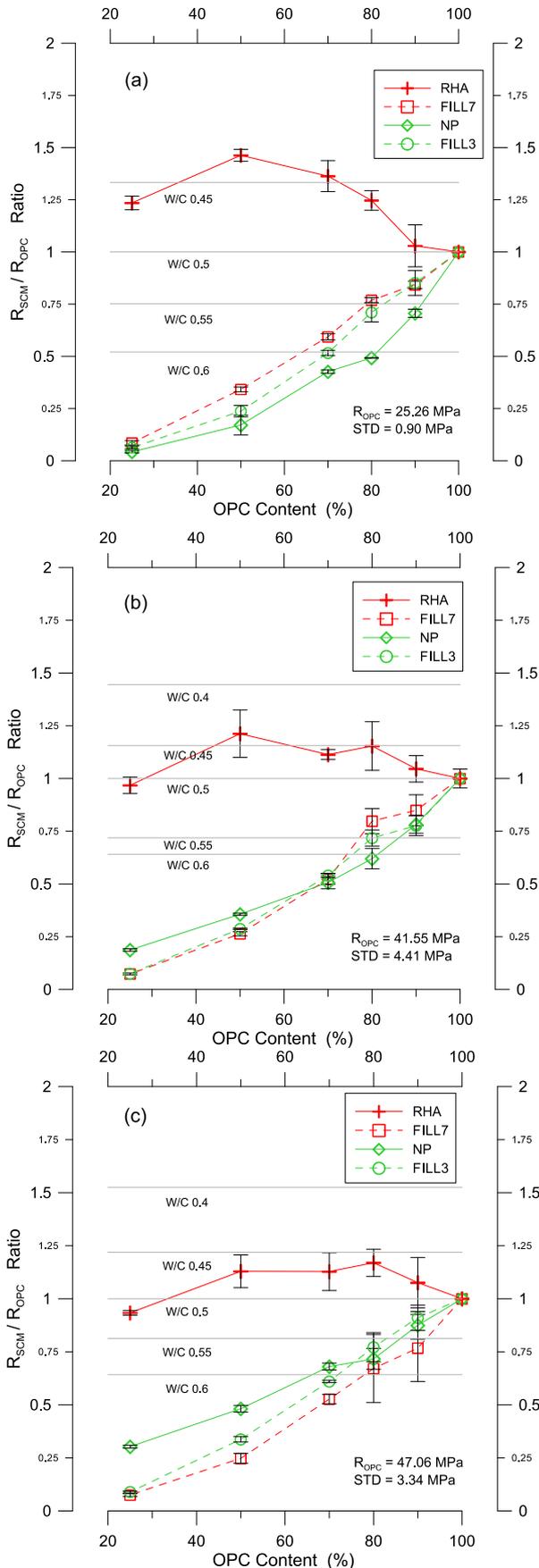


Fig. 5. Compressive strength ratios (referenced to the 100% OPC mixture) versus the OPC content in mixtures at (a) 7, (b) 28 and (c) 90 days of age.

Results at 90 days of age conform to the same trend observed between 7 and 28 days. The ongoing hydration of the OPC keeps reducing the differences in the  $R_{SCM}/R_{OPC}$  ratios between RHA and 100% OPC even though the RHA series still outperforms the 100% OPC for substitution levels up to 50% (Fig. 5c). Additionally, the NP continues to show pozzolanic activity improving its performance compared to the inert series.

Physical contribution (filler effect) of SCMs is related with particle spacing and additional nucleation sites [3,31], while chemical contribution is associated with pozzolanic reaction. In addition, finer SCMs also influence the rate of the pozzolanic reaction due to the increased contact surface with CH and water. Each of these contributions impacts compressive strength of the blended mixture in a certain amount.

Previous efforts to systematically model SCM contribution to strength (both chemically inert SCMs and pozzolanic SCMs [31,44]) have shown that these effects may be considered additive [33]. Therefore, the chemical and physical contribution of each SCM to compressive strength can be approximated as the difference between the strength obtained by the SCM and the result of the PSD-matching inert filler at the same corresponding age and substitution level. Using this approach, the RHA performance is dominated by its chemical effect at all ages, while the NP mainly contributes physically at early ages and more chemically at later ages (Fig. 5a–c).

The sizable differences in the  $R_{SCM}/R_{OPC}$  ratios between the RHA and NP can be explained by the differences in the PSD, amorphous silica content and size as derived from the PSD and WRD analyses. The smaller particle size of RHA compared to NP provides a stronger physical effect accelerating hydration, and the higher amorphous silica present in RHA compared to NP explains the higher chemical reactivity, as it was also evidenced in isothermal calorimetry results (Fig. 4).

The strength gain produced by the use of SCMs allows important cement reductions while maintaining or even improving the mechanical performance. For instance, an additional 13% by mass of cement (equivalent to a w/c reduction below 0.45 in Fig. 5a) would be needed to obtain the same 7-day compressive strength as the 50% RHA mixture with a w/cm of 0.5. Similarly, the incorporation of 20% by mass of the NP is equivalent to increasing the w/c up to 0.6. In this matter, RHA is more efficient as an OPC substitution if strength is the design parameter.

### 3.4.2. Compressive strength of mortar

The compressive strength of the mortar shows similar trends to those found in the paste (see the  $R_{SCM}/R_{OPC}$  ratios in Fig. 6). The series containing RHA as the cement substitution in general, performs better than those with 100% OPC. The series containing the NP exhibits a lower performance than those containing the RHA and 100% OPC, but still exhibits improvements with respect to the inert fillers only. The  $R_{SCM}/R_{OPC}$  ratios shown at the mortar level are, in general, lower than those observed at the cement paste level. This can be attributed to the dilution of the cementitious materials by sand [33] combined with the lack of nucleation enhancement due to the coarse PSD of the sand compared to the SCMs and OPC [45].

The  $R_{SCM}/R_{OPC}$  ratio of the RHA mortars reached approximately 1.2 at 28 and 90 days; however, at 3 days, the opposite is observed for the three substitution levels (10, 20 and 30%). This low performance can be attributed to a low availability of Portlandite from cement hydration present at such an early age to properly activate the pozzolanic reaction. Although the filler effect is predominant during the first few days [3], the RHA does show the pozzolanic effect, because its  $R_{SCM}/R_{OPC}$  ratio is higher than the ratio produced by the mixture with inert filler with a comparable PSD. This fact is also observed in the isothermal calorimetry results (Fig. 3a and b).

At later ages (i.e., 28 and 90 days), when more Portlandite is

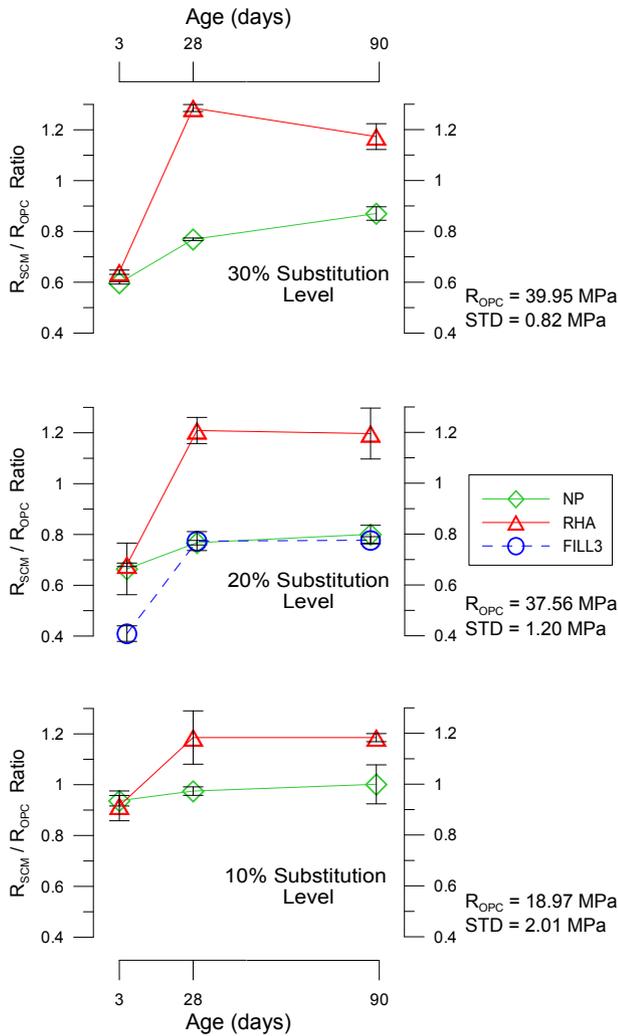


Fig. 6. Compressive strength ratios of the mortar mixtures (referenced to the 100% OPC mixture) with 10, 20 and 30% SCM substitution levels.

available, the RHA mixtures exhibited an incremental increase in the compressive strength at all levels of substitution reaching  $R_{SCM}/R_{OPC}$  ratios of approximately 1.2 and reached statistically equivalent results at 90 days for the 3 substitution levels. These results are consistent with the high reactivity observed at the paste level and agree with those previously reported for the RHA mortar [9,34].

Regarding the NP mortars, the substitution levels of 20 and 30% had  $R_{SCM}/R_{OPC}$  ratios ranging from 0.8 to 1.0 at 28 and 90 days. The low reactivity of the NP was also observed in cement pastes in a wider range of substitution levels. As concluded at the paste level, the relatively low performance of the NP might be attributed to a low amorphous silica content and coarser PSD.

At 20% substitution and 3 days of age, the NP mixtures performed better than mixtures with inert filler (FILL3) indicating a relevant pozzolanic activity. Nevertheless, at 28 and 90 days, the results for the NP inert filler mixtures are statistically equivalent, which indicates that after reaching a certain level of cement hydration, the pozzolanic activity of the NP is negligible.

### 3.5. Durability

#### 3.5.1. Chloride ion penetration

The effect of cement substitution by the SCMs was assessed at the concrete level using the rapid chloride ion penetration test

(RCPT) at 90 days of age (Fig. 7). Results are expressed as ratios of the total charge passed on each SCM mixture over the total charge passed on the 100% OPC control mixture, so the 100% OPC mixture performance is 1.0. The ASTM C1202 performance classification was also shown. A ratio below the 1.0  $R_{SCM}/R_{OPC}$  ratio represents better performance compared to the reference mixture.

There is a clear trend in the chloride permeability reduction as the substitution level of the pozzolanic SCM (RHA and NP) increases. The performance of the RHA mixtures, in this context, is statistically better than the NP, because it reduces the permeability of the reference mixture from moderate to an almost negligible and a  $RCPT_{SCM}/RCPT_{OPC}$  ratio of 0.06 with 30% substitution. This behaviour has been previously reported in several studies [18,19,21] and is an expression of the high pozzolanic activity of the rice husk ash, which has been attributed to a reduction of the interfacial transition zone (ITZ) width, porosity and portlandite content [10].

The NP mixtures have  $RCPT_{SCM}/RCPT_{OPC}$  ratios ranging from 0.7 to 0.3; a substitution level of 30% results in a very low permeability according to ASTM C1202. This is worth noting that the compressive strength suggested a relatively low gain by using NP. Performance of the NP mixture is also better than that of inert filler (FILL3), suggesting that the improvement in permeability is not only due to a physical effect but also to pozzolanic activity. The RCPT gives a more sensitive assessment than the compressive strength when assessing the SCM effect in cement based materials.

As stated by Taylor, substitutions of the OPC by inert materials, as FILL3 in this case, does not lower the degree of hydration needed to reach pore de-percolation, so it cannot reduce the overall permeability [43]. This is evident from the  $RCPT_{SCM}/RCPT_{OPC}$  ratios close to 1.0 shown by the FILL3 mixture, and explains why the permeability of this mixture is not reduced.

#### 3.5.2. Electrical resistivity

The effect of cement substitution by SCMs on the durability was assessed at the concrete level using electrical resistivity (Table 5), where an increase in the pore de-percolation produces an increase in the electrical resistivity of specimens in the saturated condition. Experimental results reveal consistent findings made when comparing the electrical resistivity to the RCPT. This can be attributed to the similarity of both tests, because the mechanism of the measurement is physically equivalent and based on the electrical properties of the material. While the sample size and pre-conditioning varies for each test, the main mechanism that controls concrete behaviour in both tests can be reduced to pore

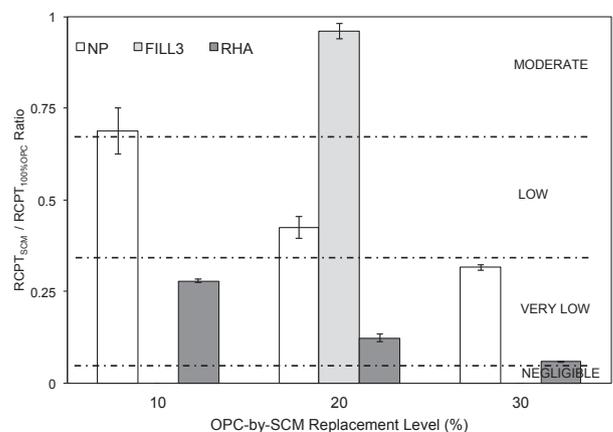


Fig. 7. Chloride ion penetration results, expressed as ratios with the 100% OPC mixture as the reference.

connectivity.

Electrical resistivity of the RHA mixtures increased approximately 3, 6 and 12 times that of the 100% OPC mixtures for substitution levels of 10, 20 and 30%, respectively. Electrical resistivity of the NP mixtures increased 2 and 3 times for substitution levels of 20 and 30%, respectively. The use of inert filler at 20% substitution reduced the electrical resistivity, which indicates an increase in the permeability. This result is similar to the findings obtained in the RCPT and capillary absorption tests, reaffirming the analysis presented by Taylor [43].

A strong correlation was found between the electrical resistivity and RCPT results. In addition, this correlation extends to the  $RCPT_{SCM}/RCPT_{OPC}$  and  $\Omega_{OPC}/\Omega_{SCM}$  ratios (Fig. 8). This allows each of these tests to be used in an almost equivalent manner to compare several substitution levels and substitution materials.

The electrical resistivity method offers clear benefits over the ASTM C1202 method. The main advantages are related to a simplified sample preparation and conditioning, greatly reduced testing time and the possibility to use the same specimen to monitor variations of measurements over time.

#### 4. Conclusions

Sustainability is and will continue to be one of the major concerns regarding concrete technology and future developments. The use of SCMs had been and still is one of the primary alternatives to reduce the carbon emissions and embodied energy while improving the durability of concrete structures. The use of these materials creates new challenges for researchers to understand the interactions occurring in cementitious systems containing these materials, to optimise the production and use of SCM and to achieve the strength and durability required by the industry.

This paper presented the characterisation of RHA and NP, a promising SCM produced from agricultural wastes and a widely used material in Chilean cements, respectively, using a multi-level approach considering the paste, mortar and concrete scales. Characterisation covered chemical and physical interaction assessments, strength of the cement paste and mortar mixtures and durability testing of the concrete samples. It was seen that the contribution of SCMs to strength is diluted when the analysis level increases and therefore, paste–aggregate interactions are introduced.

The chosen methodology, using inert fillers with different particle size distributions, allowed for decoupling the physical and chemical effects of the two SCMs studied. This improved the understanding of the contributions of the SCMs.

The main conclusions of this study are:

1. The better performance of RHA compared to NP can be attributed both to its pozzolanic reactivity due to higher amounts of amorphous silica phases and to the hydration acceleration related to its finer PSD.

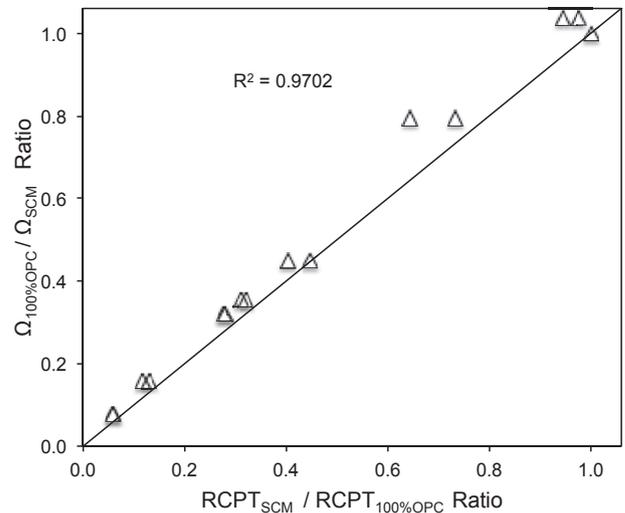


Fig. 8. ASTM C1202 chloride penetration ratios versus electrical resistivity ratios, showing a strong correlation between the results of these tests over the complete spectra of SCMs and substitution levels.

2. Substitution of the OPC by RHA increased the early age strength up to 50% and 25% for later ages. It also produced important reductions in the permeability at 90 days of age. The contribution of the RHA to the compressive strength is divided into 22% physical effect and 78% chemical effect at 90 days age and 50% substitution level. Likewise, the RHA contribution to permeability is mostly due to the chemical effects because mixtures containing inert filler had similar or higher permeability than mixtures with 100% OPC.
3. Substitution of the OPC by NP produced reductions in the early strength, which are minimised at later ages. Nevertheless, the use of NP produced considerable reductions in the permeability at 90 days. The contribution of NP to the strength can be divided into 70% physical effect and 30% chemical effect at 90 days age and 50% substitution level. Its contribution to permeability can be solely explained by the chemical effect.
4. Even considering the relatively low contribution of NP to the strength, reductions in the permeability by using NP and RHA in concrete were considerable using three different testing methods. The improvements in permeability achieved with NP and RHA were more pronounced as the substitution level increased up to 30%. Inert filler showed an inability to reduce the pore connectivity in all test results obtained. These findings showed a lower but non-negligible pozzolanic potential of the NP, as shown in the XRD results.
5. While the RHA was calcined under controlled conditions to maximise the presence of amorphous silica and thus, greatly enhance its chemical effect, NP is a natural product with a volcanic origin where no controlled temperature cycle is involved.

Table 5

Electrical resistivity of concrete samples at 90 days age.

Substitution level (%)	SCM ID	$\Omega$ Mean resistivity (Ohm·cm)	Std. Deviation (Ohm·cm)
0	–	9523	139
10	RHA	29649	1388
	NP	11977	547
20	RHA	60868	1388
	NP	21245	56
	FILL3	9179	69
30	RHA	120264	2083
	NP	26900	833

Therefore, an increase of the NP effect on concrete properties would depend only on its physical effect by further reducing its PSD.

6. Proper use of more sophisticated characterisation techniques such as XRF, XRD, Rietveld analysis, PSD and calorimetry can predict the potential of a SCM, which helps when optimising the SCM performance by changing the burning, cooling and grinding processes during manufacturing.
7. The effects of a particular SCM on concrete properties do not only depend on the physical and chemical characteristics of the SCM but also on the particular property studied. That is, the effect of a SCM on the compressive strength does not adequately predict its effect on the permeability, so independent assessments need to be performed. Furthermore, the results evidence the relevance of clearly establishing the reference frame (i.e. level of analysis and properties to be measured) prior to compare different SCM performance. In addition, the relative contribution of physical and chemical effects on compressive strength varies over time. Thus, the decoupling process should be performed at each age of interest independently.

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