Contents lists available at ScienceDirect

# **Cement and Concrete Composites**

journal homepage: www.elsevier.com/locate/cemconcomp

# Properties of mortars produced with reactivated cementitious materials

# Ricardo Serpell, Mauricio Lopez\*

Department of Construction Engineering and Management, School of Engineering, Pontificia Universidad Catolica de Chile, Santiago, Chile

### A R T I C L E I N F O

Article history: Received 19 August 2013 Received in revised form 17 July 2015 Accepted 25 August 2015 Available online 8 September 2015

Keywords: Cement recycling Concrete recycling Silica fume Fly ash Dehydrated cement paste C2S

#### ABSTRACT

The production of reactivated cementitious materials is an option for the recycling of hydrated-cementrich fines discarded during recycled aggregate production. Reactivation is based on a thermal process where calcium silicate hydrates present in the fines decompose forming new hydraulic compounds. In the reported study, materials reactivated at temperatures between 660 °C and 940 °C were characterized using X-Ray diffraction and particle size analysis, and evaluated as binders using a central composite experiment to model the effects of reactivation temperature and reactivated material substitution level on the flowability, compressive strength and expansion of mortar mixtures. Reactivation temperature effects correlated with the relative concentration of reactive phases, particularly a stabilized form of alpha'- $C_2S$  identified in the materials. Substitution effects depended on the supplementary material tested, and lacked significant interaction with reactivation temperature. In the region explored, mortars based on materials produced at 800 °C, 40% substituted by silica fume, achieved highest strength but lowest flowability.

© 2015 Elsevier Ltd. All rights reserved.

#### 1. Introduction

Concrete contributes a large fraction of the solid wastes generated in developed countries, constituting the largest single component of construction and demolition wastes [1,2]. In order to reduce the environmental impact of the construction industry, increasing amounts of concrete wastes are crushed to produce recycled aggregates for new construction works, particularly in countries with limited access to appropriate landfill areas and reduced availability of natural aggregate sources [3]. Reclamation process is based on the mechanical separation of the original aggregates from the mortar (cement paste and sand) adhered to them, which would otherwise adversely affect the fresh and hardened properties of concretes made with the recycled aggregates [4,5]. In order to obtain higher quality aggregates successive crushing stages and additional thermal or chemical processes can be combined to enhance the separation of the adhered mortar. However, as separation improves, the weight percent of crushed concrete reclaimed as aggregate decreases. In addition, since attached mortar content increases as the size fraction of the aggregate decreases [4], production is usually limited to coarse recycled aggregates. As a consequence, the largest part of the concrete wastes is transformed into fines and powder, which find little use in construction except as a backfilling material.

Due to their high concentration of residual hydrated cement paste, fines left from the production of recycled aggregates are avoided in conventional concrete mixtures [6,7]. Nevertheless, their chemical composition, also a result of their high content of hydrated cement, makes them an interesting raw material for the production of recycled cementitious materials. Through a thermal reactivation process the binding capacity of the cementitious material can be partially recovered. Dehydration of calcium silicate hydrates at temperatures over 600 °C leads to the formation of unhydrated compounds which have been described as similar in composition and structure to the dicalcium silicate present in Portland cement [8]. The rehydration of these compounds displays cementitious behavior, developing strength and thus potentially enabling the recycling of the hydrated cement wastes as a valuable construction material [9]. Using laboratory sourced pastes as raw material, Shui et al. [10] found that the maximum temperature used in the dehydration process significantly affect the water requirement for standard consistency, the degree of hydration and the compressive strength of pastes based on the reactivated material. Compressive strength was found to increase with increasing







<sup>\*</sup> Corresponding author. Vicuña Mackenna 4860, 7820436 Macul, Chile. *E-mail addresses:* rserpell@ing.puc.cl (R. Serpell), mlopez@ing.puc.cl (M. Lopez).

dehydration temperature between 300 and 800 °C. The 28-day compressive strength of pastes based on material dehydrated at 800 °C was reported to be 60% of the strength achieved by the original Portland cement paste. However, compressive strength decreased when dehydration temperature was further increased to 900 °C.

In a previous study, we investigated the main and interaction effects of nine material and process factors on the 7.28 and 90-day compressive strength of pastes based on reactivated cementitious material (RCM) [11]. Effects of factors and interactions were estimated by linear regression of results from a fractional factorial experiment in two-levels. Higher compressive strengths observed were 20.0, 32.4 and 39.0 MPa at 7, 28 and 90 days, respectively. Several material and process factors displayed significant main and interaction effects. Degree of hydration of the raw material was found to have a positive effect on the strength of RCM-based pastes, particularly at 7 days of hydration. Considering degree of hydration affects the concentration of C-S-H in the raw material, it was proposed that the main cementitious compound in the RCM is a dehydrated product of C-S-H. As expected, dilution of the raw material by inert fines of either silicate (sand) or argillaceous (bricks) composition was found to have a negative effect on strength of RCM based pastes. The extent of grinding of the raw material before the thermal treatment displayed a significant interaction effect with the presence of silica fume in the raw material. According to this interaction, increasing both the content of silica fume in the raw material and the grinding time has a positive effect on the strength of the RCM-based pastes. This was probably due to unreacted silica fume remaining in the raw material being more exposed by the longer grinding. After the thermal treatment, the remaining silica fume can participate in pozzolanic reactions with the newly formed compounds in the resulting RCM. It was found that RCMs have a substantial capacity to promote pozzolanic reactions, as indicated by the significant positive effect of partial substitution of RCM by silica fume in the new mixtures. Silica fume was selected due to its simpler chemical composition and its known pozzolanic behavior. Finally, it was found that increasing the temperature used in the reactivation process from 700 to 800 °C decreases 7-day strength but increases 28 and 90-day strength of RCM pastes. In addition, results from experiments performed at the average level of the factors evidenced significant non-linearity of the response. The source of the non-linearity could not be identified from the results of the experimental design used, as it was limited to first order effects and interactions.

The research reported in this paper continues the exploration initiated in the previous study, characterizing the effects of selected process and mixture proportioning factors over a wider range of factor levels and on a wider set of mixtures responses. Factors previously reported as having significant main and interaction effects on the strength of RCM based pastes have larger potential for optimization of the relevant properties of mixtures based on RCMs, particularly those that can be easily controlled during reactivation process or in mixture proportioning. Accordingly, the maximum temperature of the reactivation process and the level of substitution of RCM by supplementary cementitious material (SCM) in the new mixtures were selected for this second part of the study. The goal was to determine if an optimal level exists for either of them, where specific mixture responses are maximized, and to evaluate if the optimal level of either factor depends on the level of the other due to factor interaction. A central composite experimental design for two factors was selected in order to explore the factor-response relationship, estimating main, interaction and second order effects of factors.

As opposed to previous studies based exclusively on pastes, this study evaluated the performance of the RCM as a binder for the production of mortars. Consequently, selected responses were: the flow behavior, expansion and 28-day compressive strength of RCM mortars. In order to compare results with our previous study, silica fume was used as the main SCM. However, fly ash was also used to contrast the effect of silica fume on flow and strength of RCM mortars. In addition to studying the binder performance of the RCM, complementary tests were carried out in order to obtain data upon which plausible explanations for the observed behavior can be proposed. These tests included: density measurements, particle size analysis of raw and reactivated materials, XRD analysis of RCM and measurements of evaporated water during mixing of RCM pastes.

#### 2. Experimental design

Considering results from previous studies, an experimental region of interest was defined, limiting the range of reactivation temperatures and RCM substitution levels to be explored. The base range of reactivation temperatures was centered on 800 °C ± 100 °C. Pastes of RCM produced over this range of temperatures are known to develop significantly different strengths [10]. The base range of RCM substitution levels was centered on 20% + 10%. According to previous results, obtained using silica fume as the substituting material [11], the range selected extends the experimental region in the direction of increasing strength. The factor-response relationship in the selected experimental region was explored using a central composite experimental design (Fig. 1), which enables efficient use of second order regression to produce quadratic response surface models [12]. The core of the design is a full factorial experiment in two levels that allows estimation of the linear effects of factors and factor interactions (first order regression coefficients). This core is augmented with axial points, which allow estimation of the second order effects of the factors (second order regression coefficients), and central points, which allow estimation of the experimental variance of the response. The levels of the factors for the axial points were chosen according to the rotatability criteria. In response surface models derived from rotatable designs, the variance of the predicted response is a function of the distance from the center of the design only. This is a desirable feature when the behavior of the response in the experimental region is not known in advance. In central composite designs each factor is applied in five levels:  $-\alpha$ , -1, 0, 1,  $\alpha$ , where  $\alpha > 1$  is the coded level of the factor at the axial points. Choosing  $\alpha = (n_f)^{1/4}$ , where  $n_f$  is the number of factorial points in the design, a rotatable design is obtained. Therefore,  $\alpha = 1.414$  for the selected design. For execution purposes the experiment was



Fig. 1. Experimental region covered by the central composite design.

divided in two blocks: one comprising the four axial cases and two of the central cases, and one comprising the four factorial cases and the remaining two central cases. Execution of individual cases within each block was randomized. Response surface models, including first and second order coefficients, were obtained by least squares regression of experimental results. Response models for 7 and 28-day compressive strength of mortars were obtained from results from two replications of the experiment, whereas response models for mortar flow and expansion were obtained from results from a single replication.

After the main experiment was performed, three sets of additional experiments followed. One set of experiments was intended to extend the range of substitution levels explored beyond the range covered by the central composite experiment. The other two sets were meant to compare the results obtained using silica fume as the substituting material with results obtained using fly ash at different water to cementitious material ratios. The additional cases were limited to RCM produced at 800 °C.

# 2.1. Mixture design

As prescribed by the experimental program, individual mixtures incorporated RCM produced at a specific temperature and at a specific level of substitution by either silica fume or fly ash. The substitution was performed in a volumetric basis replacing a given percent of RCM by the specific amount of silica fume or fly ash having the same volume. The water content was held constant in order to fix the water to cementitious material (W/CM) volumetric ratio. Consequently, a constant volume of paste is obtained, thus fixing the paste to fine aggregate ratio and the volume of mortar produced. However, as the total weight of the cementitious material changes at the different levels of substitution the above method results in a small variation of the water to cementitious material mass ratio across the mixtures. Mixture recipes for the individual cases in the central composite experiment and in the additional experiments are shown in Tables 1 and 2, respectively. Effective water to cementitious material mass and volume ratios shown consider water absorption by the aggregate (0.6% by weight).

#### 3. Materials and methods

The wastes that serve as the raw material for the production of RCM were obtained from hydrated cement pastes made specifically for this purpose under laboratory conditions. These pastes were produced using ordinary Portland cement conforming to ASTM C150 type I, having a density of 3.140 g/cm<sup>3</sup>. In the production of the RCM mortars either silica fume or fly ash were used as SCM.

#### Table 1

Mixture proportions: cases from the central composite experiment.

Mixture proportions: additional cases.

Case	Factor levels		Mixture proportion (kg/m <sup>3</sup> )					Effective W/CM	
	R-Temp	SCM	RCM	Si fume	Fly ash	Sand	Water	Mass	Volume
C0	800	0%	432.7	0.0		1190	409.6	0.93	2.8
C13	800	40%	259.6	133.1		1190	409.6	1.02	2.8
C14	800	50%	216.4	166.4		1190	409.6	1.05	2.8
A0	800	0%	432.7		0.0	1190	409.6	0.93	2.8
A1	800	10%	389.4		34.5	1190	409.6	0.95	2.8
A2	800	20%	346.2		69.0	1190	409.6	0.97	2.8
A3	800	30%	302.9		103.5	1190	409.6	0.99	2.8
A4	800	40%	259.6		138.0	1190	409.6	1.01	2.8
A5	800	50%	216.4		172.5	1190	409.6	1.00 <sup>a</sup>	2.7 <sup>a</sup>
A6	800	60%	173.1		207.0	1190	409.6	0.98 <sup>a</sup>	2.6 <sup>a</sup>
A7	800	70%	129.8		241.5	1190	409.6	0.98 <sup>a</sup>	2.5 <sup>a</sup>
BO	800	0%	470.9		0.0	1295	362.6	0.75	2.3
B1	800	10%	423.8		36.3	1295	362.6	0.77	2.3
B2	800	20%	376.7		72.5	1295	362.5	0.79	2.3
B3	800	30%	329.6		108.8	1295	362.5	0.81	2.3
B4	800	40%	282.5		145.0	1295	362.5	0.83	2.3
B5	800	50%	235.4		181.3	1295	362.5	0.84	2.3
B6	800	60%	188.4		217.5	1295	362.5	0.84 <sup>a</sup>	2.2 <sup>a</sup>
B7	800	70%	141.3		253.8	1295	362.5	0.85 <sup>a</sup>	2.2 <sup>a</sup>

<sup>a</sup> Values account for significant bleeding observed.

Silica fume was a commercially available condensed type, composed of over 99% SiO<sub>2</sub> according to XRF analysis, and having a density of 2.307 g/cm<sup>3</sup>. Silica fume was selected as a reference SCM of known composition and pozzolanic behavior, and because it enabled comparison of results with the first phase of this study. Fly ash was obtained from a local power plant. According to the oxide analysis shown in Table 3 its chemical composition conforms to the ASTM C618 class F specification. This fly ash has a density of 2.392 g/cm<sup>3</sup>. Among the fly ashes that can be locally obtained from coal power plants, this ash was the only one conforming to class F specification. Class F was preferred in order to avoid self-cementing (or latent hydraulic) behavior to interfere in the interpretation of results. Mortars were produced using natural siliceous sand, graded as specified in Chilean standard NCh-158 (Table 4).

Source pastes were produced mixing Portland cement at 0.50 water to cement mass ratio, and cast in roughly square molds, 500 mm a side and 40 mm deep. The resulting cement paste slabs were unmolded at 24 h and placed under water for curing. At 28 days they were hammered into chunks of 40 mm maximum size, which were then placed in a drying oven at 105 °C until constant weight was achieved. A jaw crusher and a ball mill were used to

Case	Block	Factor levels				Mixture proportion (kg/m <sup>3</sup> )				Effective	
		Coded		Experimental						W/CM ratios	
		X1	X2	R-Temp	SCM	RCM	Si fume	Sand	Water	Mass	Volume
C1	1	-1.414	0	659	20%	346.2	63.5	1190	409.6	0.98	2.8
C2	1	1.414	0	941	20%	346.2	63.5	1190	409.6	0.98	2.8
C3	1	0	-1.414	800	6%	406.7	19.0	1190	409.6	0.95	2.8
C4	1	0	1.414	800	34%	285.6	107.9	1190	409.6	1.02	2.8
C5	1	0	0	800	20%	346.2	63.5	1190	409.6	0.98	2.8
C6	1	0	0	800	20%	346.2	63.5	1190	409.6	0.98	2.8
C7	2	-1	-1	700	10%	389.4	31.7	1190	409.6	0.96	2.8
C8	2	-1	1	700	30%	302.9	95.2	1190	409.6	1.01	2.8
C9	2	1	-1	900	10%	389.4	31.7	1190	409.6	0.96	2.8
C10	2	1	1	900	30%	302.9	95.2	1190	409.6	1.01	2.8
C11	2	0	0	800	20%	346.2	63.5	1190	409.6	0.98	2.8
C12	2	0	0	800	20%	346.2	63.5	1190	409.6	0.98	2.8

Table 3XRF analysis of fly ash.

	%	ASTM C 618 class F specification
Al <sub>2</sub> O <sub>3</sub>	21.0	
Fe <sub>2</sub> O <sub>3</sub>	8.31	
SiO <sub>2</sub>	55.8	
$SiO_2 + Al_2O_3 + Fe_2O_3$	85.1	70.0 min.
CaO	5.87	
MgO	2.70	
Na <sub>2</sub> O	1.54	
K <sub>2</sub> O	1.07	
TiO <sub>2</sub>	0.95	
P <sub>2</sub> O <sub>5</sub>	0.63	
SO <sub>3</sub>	0.44	5.0 max.
BaO	0.27	
SrO	0.24	
LOI	1.01	6.0 max.

reduce the material to a fine powder. To control the milling process, materials were sieved using a #200 mesh (75  $\mu$ m opening size). Milling continued until only 20% of the material was retained (average of 2 sieving tests).

Dehydration of the powdered material was performed in batches of 400 g using a programmable electric muffle oven. Heating cycle started at room temperature and proceeded at 10 °C per minute to the maximum temperature indicated by the experimental program for each batch. The material remained at the maximum temperature for 150 min, and then the oven was left to cool down to room temperature at free rate. The resulting RCMs were stored in sealed plastic containers until the date of mixture. Samples of RCMs produced were sieved to determine changes to the percentage passing the #200 mesh. In addition, particle size distributions of the Portland cement used, the powdered hydrated cement paste and the RCMs were obtained using a laser diffraction particle size analyzer (Malvern Mastersizer 2000). Reagent grade isopropyl alcohol was used as the dispersant (refractive index: 1.378). A fixed complex refractive index was used for the cementitious materials, with values 1.687 and 0.1 for the real and imaginary parts, respectively. Samples were measured in random order. Before the start of the measurement, the dispersed samples were sonicated for 120 s while circulated through the equipment using a stirrer speed of 2300 RPM. Each measurement consisted of 5 repetitions, lasting 30 s each, at 1000 frames per second. Density of RCMs was measured using a Nitrogen gas pycnometer (Ultrapyc 1200e). RCM samples were also analyzed by powder X-ray diffraction (XRD), using a Bruker D2 Phaser diffractometer, scanning between 5 and 70°.

For the production of the RCM mortars, the prescribed amount of RCM was first manually mixed with 80% of the prescribed water. The steel bowl containing the resulting paste was weighed and then placed in a water bath at room temperature. This procedure was meant to control the temperature raise of the RCM paste,

Tuble 1			
NCh-158	normalized	sand	gradation.

Table 4

Mesh opening (mm)	Sieve No	Cumulative % retained
2.00	10	0
1.68	12	5 ± 5
1.00	18	33 ± 5
0.50	35	67 ± 5
0.150	100	88 ± 5
0.075	200	98 ± 2

which can evolve a significant amount of heat of hydration in the first minutes depending on the amount of free lime present in the RCM. The paste was remixed constantly during the 5 min long water bath period. After the water bath the bowl was dried and weighed to determine the amount of water lost to evaporation. Additional water was incorporated to the mixture to compensate for the evaporated water. The sand, the silica fume or fly ash, the additional water and the rest of the prescribed water were added to the RCM paste in the bowl and mixed in a laboratory mixer until a uniform mixture was obtained ( $3 \pm 1 \min$ ).

Five mixtures were produced for each case in the central composite experiment: Two mixtures for 7-day strength testing and two mixtures for 28-day strength testing -using one of them also to measure flowability-, and one mixture for mortar expansion testing. Only one mixture was produced for each case in the additional experimental program for flowability and 28-day compressive strength testing. Flowability was measured according to procedures specified in ASTM C1437, within 1 min of the end of mixing. For strength testing purposes, the remainder of the mixture was casted in 50 mm cubic molds, and stored in a moist room at 23 °C and 100% R.H for 48 h. Specimens were then unmolded, weighed and left to cure in lime water at 23 °C until the prescribed date of testing. Strength testing was performed on the saturated surface dry specimens at a load rate of 1350 N/s (equivalent to 0.52 MPa/s). Mortar expansion was tested according to ASTM C1038. Mixtures were casted in 25 by 25 by 285 mm prism molds and stored in a moist room at 23 °C and 100% R.H. Specimens were unmolded at 48 h to avoid damage due to the low initial strength. Initial length was measured after placing them in saturated lime water at 23 °C for 30 min. Final length was measured at the age of 14 days.

# 4. Results and discussion

Mixture properties of all cases comprising the central composite experiment are shown in Table 5. As expected, the amount of water lost by evaporation during mixing of the RCM pastes varied according to the substitution level used. Increased substitution means less RCM is incorporated in a fixed volume of mixture therefore less heat is evolved. However, for mixtures incorporating the same amount of RCM the amount of evaporated water increased with increasing reactivation temperature, particularly in the range from 660 to 800 °C (Fig. 2). During the initial mixing of the RCM pastes false set was also observed. Both, the heat evolved and false set, are related to the formation of calcium hydroxide from free lime present in the RCM. During the reactivation process, free lime is first formed from the dehydration of calcium hydroxide between 400 and 550 °C. Then, when the materials reach the maximum temperature used in the process, i.e. above 550 °C, free lime is also formed from the decomposition of calcium carbonate. Since the rate of decomposition increases with increasing temperature, the amount of free lime present in the resulting RCM depends on the maximum temperature reached during the fixed length reactivation process. Whereas at 660 °C only a fraction of the calcium carbonate can decompose during the process, above 900 °C all of it is expected to be decomposed in the same time period. Consequently, the initial heat evolved by the pastes increased with increasing reactivation temperature due to increasing free lime content in the RCM. Pastes based on RCMs produced above 800 °C evolved more heat and displayed stronger false set behavior.

Factors having significant effect on the properties of the mortar mixtures were identified using analysis of variance (ANOVA) at a 5% significance level (95% confidence interval, p-values < 0.05). Effects exceeding the selected confidence interval are marked in bold in the ANOVA tables accompanying the discussion of effects. In the

Table	5		

Reculte	20202	from	tha	control	composite	evneriment
Results:	cases	IFOIII	uie	central	composite	experiment.

Case	Factor levels	Factor levels		Flow	Weight	Expansion	Compressive Strength <sup>a</sup>	
	R-Temp	Si-fume	Water	C1437	Gain	C1038	7-day	28-day
	°C	%	%	%	%	%	MPa	MPa
C1	659	20	0.54%	69.5	0.88	0.014	8.55	18.18
C2	941	20	1.16%	67.5	0.25	0.073	7.13	19.60
C3	800	6	1.90%	76.0	0.42	0.017	8.29	14.92
C4	800	34	0.85%	48.0	0.34	0.045	11.58	23.94
C5	800	20	1.08%	57.5	0.32	0.020	9.62	20.67
C6	800	20	1.24%	51.0	0.37	0.017	9.70	21.10
C7	700	10	0.74%	84.5	0.65	0.015	7.52	16.18
C8	700	30	0.58%	55.7	0.63	0.018	10.36	21.83
C9	900	10	1.70%	72.2	0.24	0.026	7.32	18.72
C10	900	30	1.01%	53.9	0.31	0.059	9.68	22.22
C11	800	20	1.08%	55.8	0.42	0.020	9.53	22.49
C12	800	20	1.16%	57.5	0.42	0.017	10.21	22.18

<sup>a</sup> 7 and 28-day strength results shown are the average of two replicates.



**Fig. 2.** Evaporated water during initial mixing versus RCM reactivation temperature (at 20% substitution level) and RCM substitution level (for RCM produced at 800 °C).

response models discussed and plotted, only these effects are included. In addition, estimated effects on flow and on compressive strength are compared to results obtained from RCM mortars where fly ash was used as the substituting material (Table 6).

# 4.1. Flow of RCM mortars

Response surface model obtained from flow test results indicates both the RCM substitution level and the temperature used to produce the RCM significantly affect the flow of RCM mortars. Table 7 shows the analysis of variance of the response model fitted, including the estimated effect of factors and their significance level (p-values). As indicated by the estimated effect of the factor (X2), in the experimental region explored, increasing the RCM substitution by silica fume decreases flow of RCM mortars. The factor also appears to have a significant second order effect (X2·X2). According to its estimated second order effect, the net effect of the substitution decreases as the substitution level increases. In the range of substitution levels covered by the response model the second order component is unable to overcome the main negative effect of the substitution, and therefore flow continues to drop as more RCM is substituted by silica fume.

According to the model, the reactivation temperature effect on flow is characterized by its second order component (X1·X1). At any substitution level, minimum flow is predicted for mortars based on RCM produced at 800 °C. From this point, either increasing or decreasing the reactivation temperature increases flow of RCM mortars (Fig. 3). Although not statistically significant, the estimated first order effect of the reactivation temperature (X1) suggests the increase in flow is higher in the direction of lower reactivation temperatures. Absence of significant interaction between the reactivation temperature and the substitution level indicates factor effects on flow are independent. According to this lack of interaction, in the experimental region explored, substitution effect on flow is largely unaffected by the varying characteristics of the RCM produced at different temperatures, and reactivation temperature effect on flow is unaffected by the level of substitution.

The effect of substitution level was observed to depend on the characteristics of the SCM used. In the additional experiments performed using fly ash as the substituting material, substitution level had the opposite effect of that previously estimated using silica fume. In fly ash incorporated RCM mortars mixed at 0.8 and 1.0 W/CM ratios flow increased as the substitution level increased (Fig. 4). These observations suggest that the effect of substitution by SCM in RCM mortars can be compared to the effect of a similar substitution in Portland cement mortars, where the impact of a given SCM on flowability depends largely on its mean particle size, density, shape, and specific surface. Whereas fly ash is usually reported to improve the rheological properties of cement pastes, mortars and concretes, the opposite has been reported for silica fume [13,14]. As in cement based mortars, differences observed in RCM mortars can be explained by the larger specific surface and smaller mean particle size of silica fume increasing water demand and cohesiveness of the mixture, respectively.

# 4.2. Strength of RCM mortars

Response surface models obtained from of 7 and 28-day test results show both RCM substitution level and reactivation temperature significantly affect compressive strength of RCM mortars (Tables 8 and 9). According to the response model fitted, at either of the tested ages, compressive strength of RCM mortars increases as substitution by silica fume is increased (X2). However, for 28-day strength the estimated effect decreases with increasing substitution level, as indicated by the significant second order effect of the factor (X2·X2). Considering both the first and second order effects estimated, the model predicts maximum strength at 28 days would be achieved at approximately 35% substitution. In additional experiments maximum 28-day strength was found at 40%

Table 6				
Results:	cases	from	additional	experiments.

Case	Factor levels		Flow	Strength
	R-Temp	Fly ash	C1437	28-day
	°C	%	%	MPa
C0	800	0	80.0	11.70
C13	800	40	a	25.80
C14	800	50	a	25.24
AO	800	0	76.3	11.50
A1	800	10	103.3	6.98
A2	800	20	108.0	7.01
A3	800	30	129.0	5.15
A4	800	40	b	3.69
A5	800	50	b	2.45
A6	800	60	b	1.40
A7	800	70	b	0.88
во	800	0	c	с
B1	800	10	20.5	17.52
B2	800	20	47.5	13.56
B3	800	30	76.5	10.22
B4	800	40	106.5	7.89
B5	800	50	121.0	5.08
B6	800	60	146.0	3.64
B7	800	70	b	1.76

<sup>a</sup> No flow.

<sup>b</sup> Exceeded flow table diameter.

<sup>c</sup> Unable to compact.

#### Table 7

ANOVA of flow test results, including estimated effect of factors.

Source	Effect (% flow)	Sum of squares	DoF	Mean of squares	F-ratio	P-Value
Average	55.45					
X1: R-Temp	-2.12	35.82	1	35.82	3.87	0.1062
X2: Si-fume	-10.84	939.57	1	939.57	101.56	0.0002
X1·X2	+2.63	27.56	1	27.56	2.98	0.1449
X1·X1	+6.86	300.85	1	300.85	32.52	0.0023
X2·X2	+3.61	83.23	1	83.23	9.00	0.0301
Blocks	+0.84	8.50	1	8.50	0.92	0.3818
Total error		46.26	5	9.25		
Total		1391.86	11			

Values in bold refer to those factors with statistical significance (p-values below 0.05).



Fig. 3. Predicted response for flow of RCM mortars at different RCM substitution levels.



Fig. 4. Flow of RCM mortars versus RCM substitution level.

#### Table 8

ANOVA of 7-day	strength test	results,	including	estimated	effect of fa	ctors.

Source	Effect (MPa)	Sum of squares	DoF	Mean of squares	F-ratio	P-Value
Average	9.77					
X1: R-Temp	-0.36	2.103	1	2.103	5.91	0.0264
X2: Si-fume	+1.23	24.279	1	24.279	68.24	0.0000
X1·X2	-0.12	0.118	1	0.118	0.33	0.5729
X1·X1	-1.00	12.872	1	12.872	36.18	0.0000
X2·X2	+0.04	0.023	1	0.023	0.06	0.8033
Blocks	-0.02	0.010	1	0.010	0.03	0.8715
Total error		6.048	17	0.356		
Total		46.216	23			

Values in bold refer to those factors with statistical significance (p-values below 0.05).

#### Table 9

ANOVA of 28-day strength test results, including estimated effect of factors.

Source	Effect (MPa)	Sum of squares	DoF	Mean of squares	F-ratio	P-Value
Average	21.61					
X1: R-Temp	+ <b>0.62</b>	6.096	1	6.096	5.82	0.0275
X2: Si-fume	+2.74	119.970	1	119.970	114.43	0.0000
X1·X2	-0.54	2.311	1	2.311	2.20	0.1559
X1·X1	-1.22	18.915	1	18.915	18.04	0.0005
X2·X2	-0.95	11.446	1	11.446	10.92	0.0042
Blocks	+0.43	4.524	1	4.524	4.32	0.0532
Total error		17.823	17	1.048		
Total		176.220	23			

Values in bold refer to those factors with statistical significance (p-values below 0.05).

substitution confirming the existence of an optimum substitution level when using silica fume as predicted by the model. In Fig. 5 the response model obtained from the main experiment (dashed line) can be compared with a second order polynomial fit of all results —from main and additional experimental— obtained for mortars based on RCM produced at 800 °C (solid line). Additional experiments also showed that the model predictions are valid only for RCM mortars where silica fume is used as the substituting material. In RCM mortars using fly ash as the substituting material 28-day compressive strength decreased as substitution level increased. This behavior was observed across the range of substitution levels explored, for mortars mixed at either 1.0 or 0.8 W/CM ratio. In the range explored these SCMs had opposite impact on strength. Although their chemical composition differs, both SCMs are high in amorphous silica. Therefore, at higher substitution levels the fly-



Fig. 5. 28-day compressive strength of RCM mortars at different RCM substitution levels.

ash would provide as much soluble silica as silica fume can at lower levels. Consequently, differences in chemical composition alone cannot explain the observed behavior. As in Portland cement based mortars, physical properties of the SCM such as its particle size significantly affect 28-day compressive strength of RCM mortars. In Portland cement based mortars where 25% of the cement is substituted by either inert or pozzolanic mineral admixtures, Lawrence et al. [15] found the effect of fineness to be significant for pozzolanic materials. Compressive strength was found to increase with increasing fineness at all ages tested. In the same study, when class F fly ash with a particle size similar to that of cement was used, compressive strength was found to decrease linearly with substitution level for hydration times up to 28 days. However, at 180 days of hydration mixtures incorporating up to 35% fly ash had developed compressive strengths exceeding the control mixture (0% replacement). Therefore, it remains to be observed how strength of RCM mortars incorporating fly ash evolves over longer hydration periods as fly ash has a lower rate of reaction and much smaller specific surface compared to silica fume.

Response surface models also show reactivation temperature significantly affects compressive strength, with a marked second order effect estimated at both testing ages (X1·X1). According to the estimated effect, increasing reactivation temperature in the range from 660 to 800 °C increases compressive strength of RCM mortars whereas increasing reactivation temperature in the range from 800 to 940 °C decreases compressive strength (Fig. 6). Lack of significant interaction effects indicate that the effect of reactivation temperature is independent of the RCM substitution level when using silica fume. Consequently, at any given substitution level, highest compressive strength is achieved using RCM produced at 800 °C.

#### 4.3. Expansion of RCM mortars

The response surface model obtained from test results indicates expansion of RCM mortars is affected by both the reactivation temperature and the substitution level used (Table 10). In the



Fig. 6. Predicted response for 7 and 28-day compressive strength of RCM mortars at different RCM substitution levels.

experimental region explored, increasing the reactivation temperature (X1) increases expansion of RCM mortars. In addition, the effect of the factor increases with increasing reactivation temperature as indicated by the significant second order effect estimated (X1·X1). As predicted by the model, expansion increases at a significantly higher rate as reactivation temperature is increased above 800 °C (Fig. 7). Increasingly higher amounts of free lime are expected to be found in the RCM produced between 800 and 940 °C due to decomposition of calcium carbonate during the reactivation process. Although the reaction of free lime with water forms larger volume Ca(OH)<sub>2</sub>, in order to produce expansion it must occur after the mortar has set. Most free lime reacts with water during mixing of RCMs. However, reaction rate is slowed down as mix water is rapidly saturated with  $Ca^{2+}$  and  $OH^{-}$  ions and  $Ca(OH)_2$  layers grow on the surface of the free lime grains. Consequently, depending on the initial concentration, a fraction of the free lime can remain unreacted after setting. In the set mortar, saturation of the pore solution with OH<sup>-</sup> ions means Ca(OH)<sub>2</sub> from the hydration of remaining free lime must be formed in situ producing expansion [16].

The estimated effect of substitution level indicates expansion of RCM mortars increases when the level of substitution by silica fume increases (X2). Generally, lower expansion is reported for silica fume incorporated pastes and concretes compared to control mixtures using pure Portland cement [17]. Nevertheless, the opposite effect has also been observed. According to Rao [18], although cement pastes without silica fume exhibited higher expansion than silica fume incorporated pastes, in the later expansion gradually increased as the content of silica fume

 Table 10

 ANOVA of Expansion results, including estimated effect of factors.



Fig. 7. Predicted response for expansion of RCM mortars at different RCM substitution levels.

increased from 5% to 30%. Likewise, Igarashi et al. [19] observed high initial expansion followed by shrinkage for silica fume incorporated mortars at low water to binder ratios (<0.30), but found that at high water to binder ratio (0.55) the expansion of silica fume incorporated mortars was almost the same as that of corresponding mortars without silica fume. Consequently, to explain the effect of silica fume substitution level on expansion of RCM mortars, an interaction between the silica fume and the RCM, different than that expected between silica fume and Portland cement, is not required. As in cement mortars, the increase in expansion observed as silica fume content is increased is believed to be caused by the reduction of the average pore size of the paste obtained as substitution levels are increased. The delayed hydration of unreacted phases, such as remaining free lime in this case, within the limited pore space available, results in internal pressure causing expansion of the mortar.

# 4.4. Characterization of RCM

According to results from sieving, the particle size of the powdered materials decreases during the reactivation process. The fraction of material retained in the 200# mesh (>75  $\mu$ m) was lower for all RCMs compared to the 20.7% average of the raw material. For RCMs the fraction retained also decreased with increasing reactivation temperature, from 15.0% for materials produced at 660 °C to 12.5%, 11.5%, 3.7% and 5.6% for materials produced at 700, 800, 900 and 940 °C, respectively. Particle size distribution analysis (Fig. 8) shows a significant reduction in the 90th percentile

Source	Effect (%)	Sum of squares	DoF	Mean of squares	F-ratio	P-Value
Average	0.017					
X1: R-Temp	+0.015	1.9E-03	1	1.9E-03	63.77	0.0005
X2: Si-fume	+ <b>0.009</b>	5.8E-04	1	5.8E-04	19.58	0.0069
X1·X2	+0.007	1.8E-04	1	1.8E-04	6.11	0.0564
X1·X1	+ <b>0.010</b>	6.2E-04	1	6.2E-04	20.92	0.0060
X2·X2	+0.004	1.1E-04	1	1.1E-04	3.65	0.1143
Blocks	-0.002	7.0E-05	1	7.0E-05	2.35	0.1859
Total error		1.5E-04	5	3.0E-05		
Total		3.5E-03	11			

Values in bold refer to those factors with statistical significance (p-values below 0.05).



Fig. 8. Particle size distribution analysis of Portland cement (OPC), raw material (hydrated cement paste, HCP), and RCM produced at 660, 700, 800, 900 and 940  $^{\circ}$ C.

equivalent volume sphere diameter (d(v, 0.9)) for the RCMs compared to the raw material, while the 10th percentile diameter (d(v, 0.1)) appears to remain largely unchanged. The consequent reduction in particle size distribution span in the RCMs continues with increasing reactivation temperature, explaining the observed reduction of material retained in the #200 mesh. In RCMs produced from 660 to 800 °C size reduction appears to affect larger particles more, as the median diameter (50th percentile) remains unchanged compared to the raw material. Conversely, RCMs produced at 900 and 940 °C exhibit lower median sizes, and significantly lower 90th percentile sizes compared to RCMs produced at lower temperatures. The reduction in the count of large particle in the RCMs compared to the raw material can be related to fractioning of larger particles during the heat cycle due to internal stresses arising from differential thermal expansion of hydrated and anhydrous phases within the particles. In addition, a reduction of specific volume is also expected due to the dehydration of hydrated phases over the whole range of reactivation temperatures explored, and due to decomposition of carbonated compounds above 800 °C. Pycnometry measurements show the average density of the RCMs is significantly higher than the density of the powdered raw material  $(2.40 \text{ g/cm}^3)$ , and appears to increase linearly with increasing reactivation temperature, from 2.81 g/cm<sup>3</sup> for RCM produced at 660 °C to 3.12 g/cm<sup>3</sup> for RCM produced at 940 °C. However, the extent to which the change in specific volume affects the particle size distribution of the RCMs remains to be studied. The significant reduction in particle size observed in materials reactivated above 800 °C can be linked to the decomposition of calcium carbonates, leading to increased concentration of CaO as discussed later in this section.

Results from XRD analysis of the reactivated materials provide clues to the cause of the observed responses. As seen in Fig. 9, two broad peaks present in the XRD scan of the RCM heated to 660 °C, roughly centered at 32.5 and 33.1°, appear with progressively higher intensity in the scans of the RCMs heated to 700 and 800 °C. They are not present in the scan of the hydrated cement paste used as raw material for the production of the RCM, where the most prominent peaks correspond to calcium hydroxide and C<sub>3</sub>S remaining unreacted at 28 days. The peaks in the 660–800 °C scans match the pattern of a stabilized form of alpha'-C<sub>2</sub>S, a high temperature polymorph of the dicalcium silicate. Although best matching pattern corresponds to alpha'-Ca<sub>2</sub>SiO<sub>4</sub> 0.05-Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>



Fig. 9. XRD scans of RCM produced at different reactivation temperatures. Dashed lines indicate positions of principal alpha'-C<sub>2</sub>S reflections.

(PDF2 database reference code: 00-049-1674), it is not possible to determine if the stabilizing agent is phosphate or other chemical species with the information gathered in this study alone. Stabilization of more reactive, high temperature polymorphs of  $C_2S$  is possible with a range of different dopants, such as alkalis, sulfur and barium additions, as has been shown in extensive research oriented at developing active Belite-based cements [20,21]. Nevertheless, the match supports the identification of alpha'- $C_2S$ , which is also compatible with the raw materials and temperatures involved in the reactivation process. In the scan of the RCM produced at 900 °C the referred peaks appear in a shifted position and with decreased intensity. Consequently, the alpha'- $C_2S$  pattern no longer matches

the profile. Peak position and intensity continues to change with increasing temperature. For RCM produced at 940 °C the beta-C<sub>2</sub>S (Larnite) pattern best matches the profile in the same region.

According to Taylor [22], when the hydration products of Portland cement are decomposed at temperatures between 800 and 1000 °C, beta- $C_2S$  is the normal product. However, since alpha'- $C_2S$ forms at temperatures around 630–680 °C, it must be present in all the materials during the high temperature phase of the reactivation process. The fact that it remains stable at ambient temperature only in the materials that were heated up to 800 °C or less could mean the stabilizing agent is removed from the structure at higher temperatures. Using the data gathered in the reported research alone it is not possible to determine if this happens because the stabilizing agent is a volatile compound, or because it is taken up by other phase formed at the higher temperature, or because it is exsolved on cooling when the structure was formed at a higher temperature.

The relative XRD intensities of several interest phases as observed in RCMs produced at different temperatures are shown in Fig. 10. Intensities were normalized relative to the highest intensity observed for each particular phase. Therefore, the graph represents the evolution of each phase as reactivation temperature is changed, but not the relative abundance of phases at any given temperature. Intensity of free lime was determined from the height of the peak at an angle of 37.36°. Intensity of alpha'-C<sub>2</sub>S was determined from the height of the peaks at 32.45 and 33.11°. Intensity of beta-C<sub>2</sub>S was determined from the height of the peaks at 32.09, 32.59 and 34.32°. As expected, free lime is seen to increase intensity at a higher rate in the range from 800 to 900 °C where the calcium carbonate decomposes at a higher rate. As temperature increases, progressive dehydration of C-S-H leads to formation of increasing amounts of high temperature crystalline phases. If all alpha'-C2S produced were to remain stable to room temperature increasing amounts would be identified with increasing temperature in all the range explored. In the range from 660 to 800 °C, alpha'-C<sub>2</sub>S increases with increasing temperature. Conversely, in the range from 800 to 940 °C, alpha'-C<sub>2</sub>S decreases with increasing temperature. In this later range Beta-C<sub>2</sub>S is seen to increase at a higher rate with increasing temperature. Consequently, alpha'-C<sub>2</sub>S produced from the dehydration of C–S–H at up to 800 °C appears to remains stable on cooling, whereas when the same phase is heated to higher temperatures progressively more of it appears to revert to beta-C<sub>2</sub>S on cooling.

Identification of a stabilized form of alpha'-C<sub>2</sub>S is compatible with the strength observations, as it is known to react much faster than beta-C<sub>2</sub>S, gaining strength at a higher rate over a period of several months [23,24]. Therefore, 28-day compressive strength increases as the reactivation temperature of the RCM is increased from 660 to 800 °C, due to increasing content of alpha'-C<sub>2</sub>S in the reactivated materials. Conversely, 28-day compressive strength decreases as the reactivation temperature of the RCM is increased



Fig. 10. Relative intensity of interest phases identified in the XRD scans of the RCM produced at different reactivation temperatures.

from 800 to 940 °C, due to increasing amount of alpha'-C<sub>2</sub>S reverted to beta-C<sub>2</sub>S in the materials.

### 4.5. Optimization of mortar properties

According to the response models derived, compressive strength, flow and expansion of RCM mortars cannot be simultaneously optimized using only the studied factors. Adjusting either the reactivation temperature or the silica fume substitution level to maximize compressive strength minimizes flow. At any substitution level, optimal 7-day and 28-day strengths are predicted for mortars based on RCM reactivated at ~780 °C and ~825 °C, respectively. Predicted flow for these mortars is within 1% of the minimum value predicted at any substitution level (predicted for mortars based on RCM reactivated at 800 °C). In order to optimize compressive strength while still achieving minimum workability a plasticizing admixture would be required when using silica fume as a SCM. Alternatively, fly ash could be used instead of silica fume, increasing the flow of mortar as substitution level increases. However, up to 28 days, increasing the fly ash substitution level was observed to decrease compressive strength of RCM mortars. At any silica fume substitution level, lower expansion is predicted for mortars based on RCM reactivated at ~725 °C. However, for mortars achieving maximum strength, based on RCM reactivated at ~800 °C, predicted expansion is still under 0.02% when silica fume substitution level is limited to 20% or less.

# 5. Conclusions

Fresh and hardened properties of mortars based on reactivated cementitious materials (RCM) are significantly affected by the reactivation temperature used to produce the RCM and by the level to which it is substituted by a supplementary cementitious material (SCM) in the mortar mixture. Response models developed in this study indicate these factors do not have interaction effects on flow, compressive strength and expansion of RCM mortars and, accordingly, their main effects can be analyzed independently.

#### 5.1. Substitution level

Substitution of RCM by a suitable SCM can decrease the concentration of free lime in the mixture, thus decreasing the initial heat and the false set behavior as the substitution level increases. The general effect of the substitution by SCM in RCM mortars was found to be comparable to the effect of similar substitutions in Portland cement based mortars. As in cement based mortars, flow of RCM mortars can be adjusted by varying the substitution level of the SCM. When substituting RCM by silica fume, flow decreases with increasing substitution level. Conversely, when substituting RCM by class F fly ash, flow increases with increasing substitution level. Likewise, strength of RCM mortars is affected by the substitution level depending on the type of SCM used. When substituting RCM by fly ash 28-day compressive strength decreases with increasing substitution. Conversely, when substituting RCM by silica fume strength increases with increasing substitution until reaching an optimum level. In this study, maximum strength was achieved at 40% substitution by silica fume. Finally, expansion of RCM mortars was studied using silica fume as the substituting material. In the range of substitution levels explored, expansion increases as the substitution by silica fume increases.

#### 5.2. Reactivation temperature

Performance of the RCM as a binder for mortars is affected by the relative abundance and chemical composition of its phases, which are, in turn, a result of the temperature history of the reactivation process. Among the phases identified in the XRD of the RCMs produced in this study, the contents of free lime and of two polymorphs of dicalcium silicate, beta- $C_2S$  and a stabilized form of alpha'- $C_2S$ , are seen to evolve with reactivation temperature.

Free lime content in the RCM increases with increasing reactivation temperature. The rate of increase is higher above 800 °C due to faster decomposition of calcium carbonate. Hydration of free lime evolves a significant amount of heat and can produce false set behavior. Consequently, the heat evolved and the false set behavior of RCM increase with increasing reactivation temperature. Likewise, delayed hydration of free lime remaining in the set mortar is a source of expansion, and thus, expansion of RCM mortars increases with increasing reactivation temperature, particularly for materials produced above 800 °C.

Depending on the reactivation temperature used, alpha'-C<sub>2</sub>S produced from the decomposition of calcium silicate hydrates above 600 °C can remain stable at ambient temperature in the RCM. Between 660 and 800 °C, alpha-C<sub>2</sub>S content in the RCM increases with increasing reactivation temperature. Conversely, above 800 °C alpha'-C<sub>2</sub>S content decreases with increasing reactivation temperature, partially reverting to beta-C<sub>2</sub>S on cooling. Strength developed by RCM mortars at 7 and 28 days is significantly affected by alpha'-C<sub>2</sub>S content. Consequently, in order to maximize 28-day strength, a RCM having the largest content of alpha'-C<sub>2</sub>S must be obtained by careful selection of the reactivation temperature. The effect of reactivation temperature on flow of RCM mortars is the opposite as its effect on strength. Minimum flow is obtained using RCM produced at 800 °C which has the highest alpha'-C<sub>2</sub>S content. Therefore, in order to obtain a workable mortar and at the same time maximize strength, plasticizing admixtures would be required.

#### Acknowledgments

We acknowledge support from the Chilean National Commission for Scientific and Technological Research, CONICYT, through FONDAP project 15110020, and particularly from Professor Pablo Pasten of the Department of Hydraulic and Environmental Engineering at Pontificia Universidad Catolica de Chile. We express our gratitude to Mr. Iván Navarrete of the Department of Construction Engineering and Management, Mr. Patricio Pérez from the Metallurgy Laboratory of the Department of Mechanical and Metallurgical Engineering, and the staff at the Materials Strength Laboratory, RESMAT, all of them from the School of Engineering of Pontificia Universidad Católica de Chile.

# References

- C. Meyer, The greening of the concrete industry, Cem. Concr. Compos. 31 (2009) 601–605, http://dx.doi.org/10.1016/j.cemconcomp.2008.12.010.
- [2] V.W.Y. Tam, C.M. Tam, A review on the viable technology for construction waste recycling, Resour. Conserv. Recycl. 47 (2006) 209–221, http:// dx.doi.org/10.1016/j.resconrec.2005.12.002.
- [3] J.M.C. Lopes de Brito, A.P. Gonçalves, J.R. dos Santos, Recycled concrete

production: multiple recycling of concrete coarse aggregates, Rev. Ing. Construcción 21 (2006) 33-40.

- [4] M. Sanchez de Juan, P. Alaejos Gutiérrez, Study on the influence of attached mortar content on the properties of recycled concrete aggregate, Constr. Build. Mater. 23 (2009) 872–877, http://dx.doi.org/10.1016/j.conbuildmat.2008.04.012.
- [5] A. Shayan, A. Xu, Performance and properties of structural concrete made with recycled concrete aggregate, ACI Mater. J. 100 (2003) 371–380.
- [6] J.M. Khatib, Properties of concrete incorporating fine recycled aggregate, Cem. Concr. Res. 35 (2005) 763–769, http://dx.doi.org/10.1016/ j.cemconres.2004.06.017.
- [7] S. Kenai, F. Debieb, L. Azzouz, Mechanical properties and durability of concrete made with coarse and fine recycled aggregates, in: R.K. Dhir, T.D. Dyer, J.E. Halliday (Eds.), Sustain. Concr. Constr. Proc. Int. Conf. Held Univ. Dundee, Scotland, UK 9-11 Sept, 2002, Thomas Telford, London, 2002, pp. 383–392.
- [8] C. Alonso, L. Fernandez, Dehydration and rehydration processes of cement paste exposed to high temperature environments, J. Mater. Sci. 39 (2004) 3015–3024.
- [9] Z. Shui, D. Xuan, H. Wan, B. Cao, Rehydration reactivity of recycled mortar from concrete waste experienced to thermal treatment, Constr. Build. Mater. 22 (2008) 1723–1729, http://dx.doi.org/10.1016/j.conbuildmat.2007.05.012.
- [10] Z. Shui, D. Xuan, W. Chen, R. Yu, R. Zhang, Cementitious characteristics of hydrated cement paste subjected to various dehydration temperatures, Constr. Build. Mater. 23 (2009) 531–537, http://dx.doi.org/10.1016/ j.conbuildmat.2007.10.016.
- [11] R. Serpell, M. Lopez, Reactivated cementitious materials from hydrated cement paste wastes, Cem. Concr. Compos. 39 (2013) 104–114, http:// dx.doi.org/10.1016/j.cemconcomp.2013.03.020.
- [12] G.E.P. Box, K.B. Wilson, On the experimental attainment of optimum conditions, J. R. Stat. Soc. Ser. B Stat. Methodol. 13 (1951) 1–45.
- [13] C.F. Ferraris, K.H. Obla, R. Hill, The influence of mineral admixtures on the rheology of cement paste and concrete, Cem. Concr. Res. 31 (2001) 245–255, http://dx.doi.org/10.1016/S0008-8846(00)00454-3.
- [14] G.A. Rao, Investigations on the performance of silica fume-incorporated cement pastes and mortars, Cem. Concr. Res. 33 (2003) 1765–1770, http:// dx.doi.org/10.1016/S0008-8846(03)00171-6.
- [15] P. Lawrence, M. Cyr, E. Ringot, Mineral admixtures in mortars effect of type, amount and fineness of fine constituents on compressive strength, Cem. Concr. Res. 35 (2005) 1092–1105, http://dx.doi.org/10.1016/ j.cemconres.2004.07.004.
- [16] M. Deng, D. Hong, X. Lam, M. Tang, Mechanism of expansion in hardened cement pastes with hard-burnt free lime, Cem. Concr. Res. 25 (1995) 440–448.
- [17] M. Mazloom, A.A. Ramezanianpour, J.J. Brooks, Effect of silica fume on mechanical properties of high-strength concrete, Cem. Concr. Compos. 26 (2004) 347–357, http://dx.doi.org/10.1016/S0958-9465(03)00017-9.
- [18] G.A. Rao, Influence of Silica fume replacement of cement on expansion and drying shrinkage, Cem. Concr. Res. 28 (1998) 1505–1509.
- [19] S. Igarashi, H.R. Kubo, M. Kawamura, Long-term volume changes and microcracks formation in high strength mortars, Cem. Concr. Res. 30 (2000) 943–951, http://dx.doi.org/10.1016/S0008-8846(00)00251-9.
- [20] K. Morsli, Á.G. de la Torre, M. Zahir, M.A.G. Aranda, Mineralogical phase analysis of alkali and sulfate bearing belite rich laboratory clinkers, Cem. Concr. Res. 37 (2007) 639–646, http://dx.doi.org/10.1016/ j.cemconres.2007.01.012.
- [21] K. Morsli, Á.G. de la Torre, S. Stöber, A.J.M. Cuberos, M. Zahir, M.A.G. Aranda, Quantitative phase analysis of laboratory-active belite clinkers by synchrotron powder diffraction, J. Am. Ceram. Soc. 90 (2007) 3205–3212, http:// dx.doi.org/10.1111/j.1551-2916.2007.01870.x.
- [22] H.F.W. Taylor, Cement Chemistry, second ed., Thomas Telford, London, 1997.
- [23] M.Y. Benarchid, A. Diouri, A. Boukhari, J. Aride, I. Elkhadiri, Hydration of iron-phosphorus doped dicalcium silicate phase, Mater. Chem. Phys. 94 (2005) 190-194, http://dx.doi.org/10.1016/j.matchemphys.2005.04.047.
- [24] A.J.M. Cuberos, A.G. De la Torre, M.C. Martín-Sedeño, L. Moreno-Real, M. Merlini, L.M. Ordónez, et al., Phase development in conventional and active belite cement pastes by Rietveld analysis and chemical constraints, Cem. Concr. Res. 39 (2009) 833–842, http://dx.doi.org/10.1016/ j.cemconres.2009.06.017.