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RESISTANCE TO SALTS OF LIME AND POZZOLAN MORTARS

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Abstract

This paper presents and analyses the results of chlorides and sulphates resistance tests of lime and pozzolan mortars (1:1:4, hydrated lime:pozzolanic component:river sand, in volume) which seemed to be efficient for historic buildings and correlate them with other characteristics involved, as the cases of porosity, mechanical resistances and hydraulic compounds development.

1. Introduction

The functional requirements of mortars to be applied on historic buildings depend on multiple conditions and require several characteristics that are not always easy to achieve and harmonize. Fundamentally these mortars should allow an efficient protection to the substrates on which they are applied, in order to avoid the development of processes that may lead to degradation. They have to present good mechanical, physical and chemical compatibility with the masonries and simultaneously they must achieve minimum characteristics to prevent their own degradation, particularly in the case of soluble salts.

In order to allow a better knowledge and an easier use of lime mortars for the conservation of historic buildings a research program has been carried out in which the effects of pozzolanic components on lime mortars were evaluated. The aim was to improve the characteristics and the performance of these products [1].

In the previous work refered different pozzolanic components were used and characterized. For comparison with a pure lime mortar three compositions were prepared with each of the different pozzolanic components, maintaining the proportion in volume of one part of binder (hydrated lime plus pozzolanic component) and two parts of the same river sand (1:0,5:3, 1:1:4, 1:1,5:5). All the fresh mortars presented comparable flows. The samples were cured for two months on dry and on saturated ambiences. For each type of mortar/curing conditions several samples were prepared.

Appropriate tests were carried out in order to determine the characteristics obtained with different components used in the mortars, their proportions and curing conditions (water retentivity of fresh mortars, linear shrinkage, adhesion, dynamic modulus of elasticity, flexural and compressive strength, carbonation rate, bulk density and open porosity, water vapour permeability, soluble salts and Ca^{++} approximate content, thermal analysis and scanning electron microscopy examination, capillary water absorption, chloride and sulphate resistance [2, 3]. A great importance was given to these last tests since salt resistance is a fundamental issue for the durability of historic buildings renders.

The present paper presents and analyses the results of the chlorides and sulphates resistance tests of the lime and pozzolanic components mortars of the intermediate composition (1:1:4, hydrated lime:pozzolanic component:river sand, in volume, which seemed to be the most efficient for rendering mortars of historic buildings among the studied mortars) and correlates them with other characteristics namely flexural and compressive strength and open porosity of the mortars, microstructure observed under SEM in terms of CSH growth (when possible) and pozzolanic reactivity of the components used.

2. Experimental work

2.1 Preparation of the material

The sand used was river sand from the same lot (to exclude the variability due to this material) – **sand**. The lime used was hydrated lime commercialised in powder in the Portuguese market – **lime**. The pozzolan used was natural powder pozzolan from the Stº. Antão island (Cabo Verde Republic) – **poz**. The fly ashes used were an industrial by-product used in powder by the cement factories – **fly**. The ceramic material used was obtained by the powder collectors in a ceramic bricks factory, before the firing process. It was then fired for 3,5 hours at 600ºC (**cer600**) and 800ºC (**cer800**) and for 30 minutes at 700ºC (**cer700”**). The kaolin from Alvarães (Viana do Castelo region) was crushed and sieved. The material used passed the nº30 ASTM sieve. It was then fired for 3,5 hours at 600ºC (**kao600**) and at 800ºC (**kao800**) and for 30 minutes at both 600ºC and 800ºC (**kao600”** and **kao800”).**

2.2 Preparation of the mortar samples

The mixture of the mortars components was mechanical and always identical. The samples were mechanically compacted in two layers. For the mortars preparation a comparable flow was always reached [4]. The samples have been subjected to one of two different types of cure until the age of test (60 days): 23 ± 3ºC and 50 ± 5% RH – dry cure **D**; in a closed plastic bag until the age of demoulding and in a closed environment with saturated ambience until the age of test – humid cure **H**.

Testing program and results

All the mortar samples (dry and humid cures) were dried to constant mass at 60ºC just before the age of testing (60 days). The flexural and compressive strength as well as the open porosity were evaluated from three of the 4x4x16 cm^3 samples of each mortar. Other three 4x4x16 cm^3 samples were cut in half (by a flexural test) and first used for the determination of capillary water absorption [4]. After dried until constant mass again, three half samples were subjected to the chloride crystallisation test and the other three to the sulphates resistance test. When the thermal measurements and the SEM examination of some of the mortar samples were conducted, these mortars had between one and two years old.

Table 1 presents the mortars designation (type of pozzolanic component and type of cure), their formulation (1:1:4 - hydrated lime:pozzolanic component:river sand, in volume) and the obtained flow. Each mortar is identified by the pozzolanic component used and the type of cure (D - dry or H - humid). **Lime0** is the control mortar.

Table 1 – Mortars designation, formulations (in volume) and flow

Mortar	**lime0**	**poz**	**fly**	**cer600**	**cer800**	**cer700"**	**kao600**	**kao800**	**kao600"**	**kao800"**	**sand**	**flow**
lime0	1										2	67
poz D	1	1									4	67
poz H	1	1									4	69
fly D	1		1								4	70
fly H	1		1								4	70
cer600 D	1			1							4	70
cer600 H	1			1							4	74
cer800 D	1				1						4	77
cer800 H	1				1						4	70
cer700"D	1					1					4	69
cer700"H	1					1					4	70
kao600 D	1						1				4	72
kao600 H	1						1				4	72
kao800 D	1							1			4	74
kao800 H	1							1			4	71
kao600"D	1								1		4	68
kao600"H	1								1		4	68
kao800"D	1									1	4	67
kao800"H	1									1	4	67

2.2.1 Reactivity of the pozzolanic components

The reactivity of the pozzolanic components was evaluated by the use of EN 196-5 [5] on samples in accordance with NP 4220 [6], of 75% of Portland cement type I 42,5 R and 25% of the pozzolanic component.

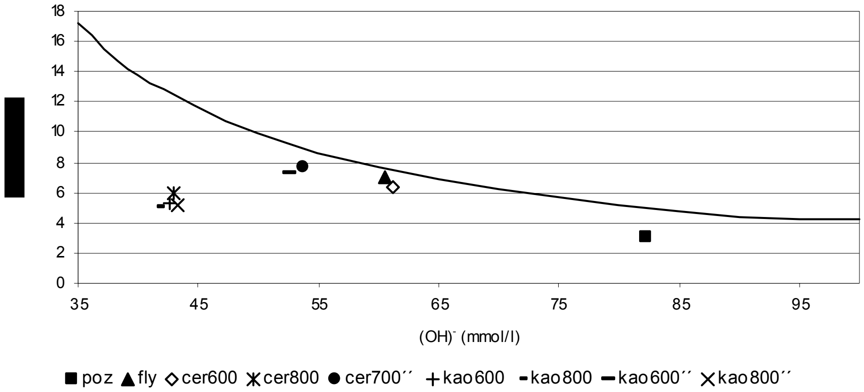

Fig. 1 – Evaluation of pozzolanic reactivity

As it can be seen in fig. 1, where the CaO versus $(OH)^-$ contents of the pozzolanic component is presented, for a temperature of 40ºC, and comparatively with the curb that correspond to the saturated content in calcium oxide, the artificial pozzolans submitted to thermal treatment for a longer period (3,5 hours) and/or to high temperature generally present higher pozzolanic reactivity (cases of **cer800**, **kao600**, **kao800** and **kao800”**). The pozzolanic components identified by **kao600”**, **cer700”**, **cer600** and **fly** present similar pozzolanic reactivity, not as high as the previous components. The natural pozzolan (**poz**) present a lower reactivity. The data of some of the pozzolanic components are qualitatively summarized in table 3.

2.3.2 Flexural and compressive strength and open porosity

Flexural strength values were determined based on three points flexural test and compressive tests were done with the resultant half samples, according to Fe 27 UNL/FCT [4]. The tests for determination of the open porosity were performed based on standard procedures by total saturation with water under vacuum and the hydrostatic weight method, following the Fe 02 UNL/FCT [4]. Table 2 presents the flexural and compressive values and the open porosity of the samples.

2.3.3 Resistance to chlorides

The test for the evaluation of the resistance to chlorides was performed immersing three half samples of each mortar (dried to constant mass at 105ºC after being used in the capillarity test) in a saturated sodium chloride solution for 24 hours, after which they were dried again until constant mass. By the difference between the dry masses of each sample after and before immersion it was possible to determine the quantity of retained chlorides, in terms of percentage of the initial dry mass. The samples were then placed in a climatic chamber where they were exposed to repeated cycles of 12 hours at 90% RH and 12 hours at 40% RH, with a constant temperature of 20ºC. Until 50 cycles were reached, the samples were weighed every week to determine the mass variation that occurred, according to Fe 12 UNL/FCT [4]. The deterioration of the samples generally occurred by development of superficial disaggregation of the material, as can be seen in fig. 2. Table 2 presents the results from the chlorides resistance test in terms of percentages of retained chlorides and of mass variation after 30 and 50 cycles and fig. 3 plots the percentage of mass variation as a function of the number of cycles.

2.3.4 Resistance to sulphates

To evaluate the sulphate resistance three half samples of each mortar (after being submitted to the capillarity test) were dried to constant mass. They were then immersed in a 6% anidrous sodium sulphate solution for 2 hours and then dried again for about 21 hours at 105ºC, after what they were weighed again to determine the mass variation and their integrity visualised. These cycles of immersion, drying and weighing were repeated until the destruction of the sample or 25 cycles were completed, following the Fe 11 UNL/FCT [4]. The destruction of some of the samples occurred by internal rupture of the material, as can be seen in fig. 4. The results in terms of the percentage of mass variation after 5, 15 and 25 cycles are presented in table 2 and fig. 5 plots the percentage of weight variation as a function of the number of cycles.

2.3.5 Observed microstructure in terms of calcium silicate hydrates [3]

The samples for SEM examination were gold-palladium sputter coated. The thermal measurements were carried out in air, at a rate of 10ºC/min, from room temperature to 1200ºC. The thermal analysis and the SEM examination have only been done on some of the mortars. Although in the thermal analysis the dehydration of the hydraulic components appears in the same temperature range, their appearance differs when observed by SEM, as can be seen in fig. 6.

The different appearance can be attributed to the compositional variation of the pozzolanic materials, which result in the crystallization of hydraulic compounds (typically CSH).

Fig. 2 – Chlorides resistance test: samples in the climatic chamber and deterioration of the samples

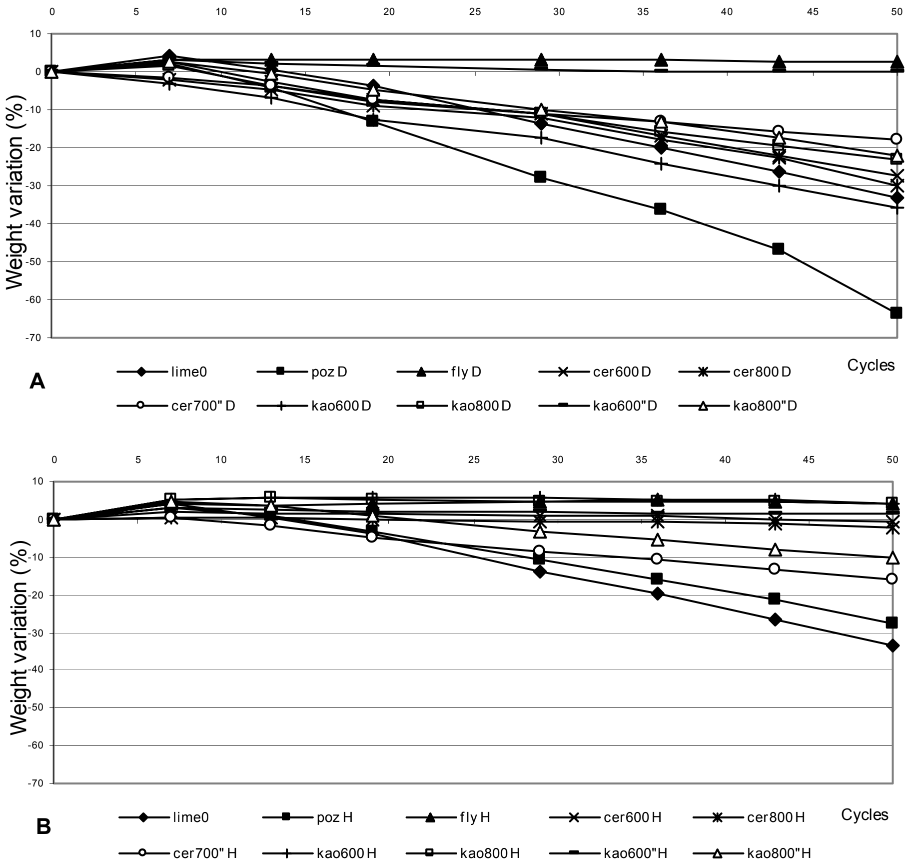

Fig. 3 – Chlorides resistance test (A – dry cure samples; B – humid cure samples)

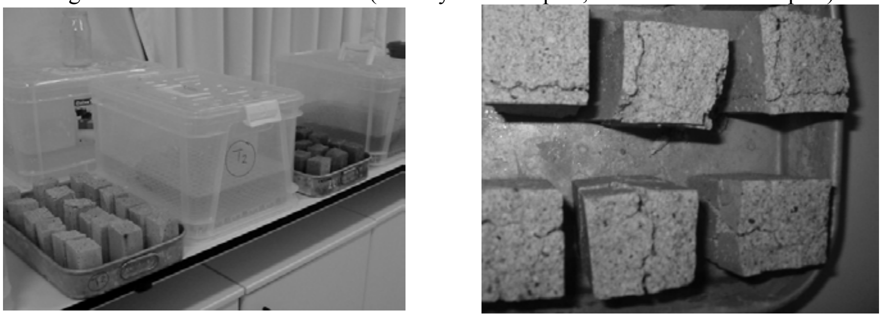

Fig. 4 – Sulphates resistance test: samples for immersion and general deterioration of the samples

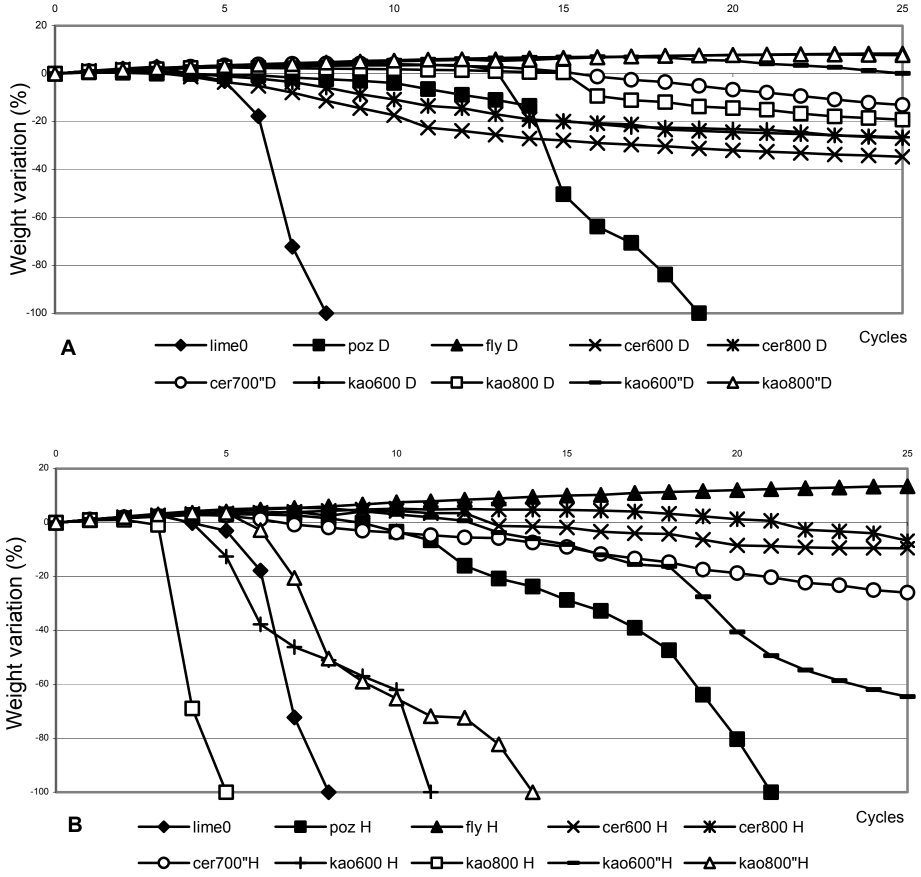

Fig. 5 – Sulphates resistance test (A –dry cure samples; B – humid cure samples)

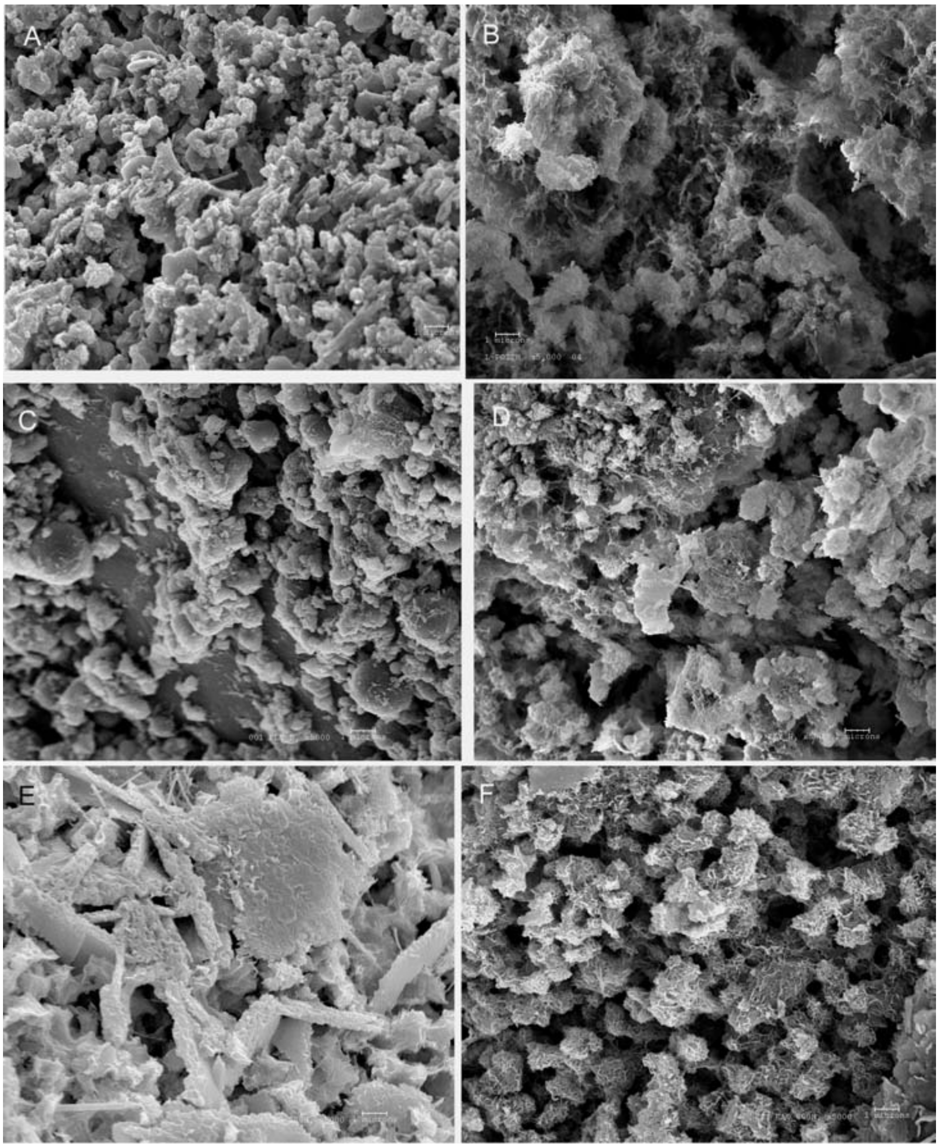

Fig. 6 – SEM photomicrographs of fracture surfaces of lime based mortars with different pozzolanic materials (5000x; A – lime0; B – poz H; C – fly D; D – fly H; E – cer800 H; F – kao800 H) [3]

The influence of the pozzolanic components can be seen between fig. 6 A and fig. 6 B to F. The sample containing natural pozzolan (humid cure) shows an uniform coating of very fine needles on most particles (fig. 6 B). The influence of curing conditions is illustrated for the case of mortars containing fly-ash, where the sample submitted to humid cure shows a higher proliferation of typical fibrous CSH crystals growth as compared to a dry cure sample, where the growth can be seen starting on the surface of the fly-ash particles (fig. 6 C and D). For the clay containing mortars, only those with clays fired to 800ºC and cured in humid conditions were examined. For the case of the mortar with fired ceramic material, the growth of the CSH crystals results in some few larger fibrous crystal clumps with smaller growth beginning on the surface of the clay particles (fig. 6 E). For the mortar with fired kaolin, a more uniform and denser growth covers the surface of the particles (fig. 6 F) [3]. The data in terms of development of CSH are qualitatively summarized in table 3.

Table 2 – Open porosity, mechanical and salts resistance of the mortars

Mortar	**Open Poros. (%)**	**Flex.R. (MPa)**	**Compr.R. (MPa)**	**Retain. Chlor. (%)**	**Chlor.Resist. (%w.variat.)**		**Sulph.Resist. (%w.variat.)**		
					30 c.	**50 c.**	**c.5**	**c.15**	**c.25**
lime0	34	0,33	0,70	4,4	-13,9	-33,4	-3,0	-100(8º)	
poz D	32	0,14	1,01	-	-29,7	-63,7	-0,4	-50,4	-100(19º)
poz H	36	0,17	1,27	5,6	-11,7	-27,7	3,1	-28,8	-100(21º)
fly D	29	0,27	0,67	3,3	2,9	2,5	2,9	6,6	8,4
fly H	31	0,52	2,44	4,1	4,5	4,2	4,1	10,0	13,5
cer600 D	34	0,24	1,10	4,5	-11,1	-27,6	-3,6	-28,0	-34,8
cer600 H	36	0,20	2,04	4,9	1,0	-0,6	3,2	-1,9	-9,5
cer800 D	33	0,36	1,39	4,1	-12,0	-29,8	-1,1	-20,0	-27,0
cer800 H	35	0,22	2,20	4,7	-0,4	-2,4	3,4	4,7	-6,7
cer700"D	33	0,20	0,36	3,5	-11,3	-18,1	3,4	0,8	-13,1
cer700"H	35	0,08	0,53	4,6	-8,3	-15,8	2,6	-9,1	-26,0
kao600 D	33	0,68	3,82	4,3	-17,3	-35,6	3,2	-19,8	-26,6
kao600 H	34	0,80	6,98	5,1	5,6	4,2	-12,7	-100(11º)	
kao800 D	34	0,48	2,88	4,6	-11,2	-23,4	2,7	0,5	-19,2
kao800 H	33	1,07	8,00	4,9	5,0	4,1	-100,0		
kao600"D	33	0,22	0,52	3,8	0,6	-0,1	3,5	6,9	0,1
kao600"H	35	0,09	0,58	4,8	1,8	1,7	4,9	-8,1	-64,5
kao800"D	35	0,40	1,23	3,9	-10,2	-22,0	3,2	6,4	7,8
kao800"H	35	0,49	4,20	5,9	-3,5	-10,2	3,6	-100(14º)	

The number inside ( ) in the sulphates resist. values indicate the cycle where the mortar samples destruction occurred.

3. Discussion

The chart in fig. 7 presents the open porosity, the flexural and compression resistances and the resistance to salts (in terms of weight variation) of the analysed mortars.

Table 3 – Development of CSH of the mortars and pozzolanic reactivity of the component

Mortar	CSH growth	Pozzolanic react.
poz H	+++	+
fly D	+	+++
fly H	(+)++	+++
cer800 H	(++)+	+++++
kao800 H	++++	++++++

More quantity of + symbols indicate more intensity of the analysed characteristic
( ) indicate longer crystals

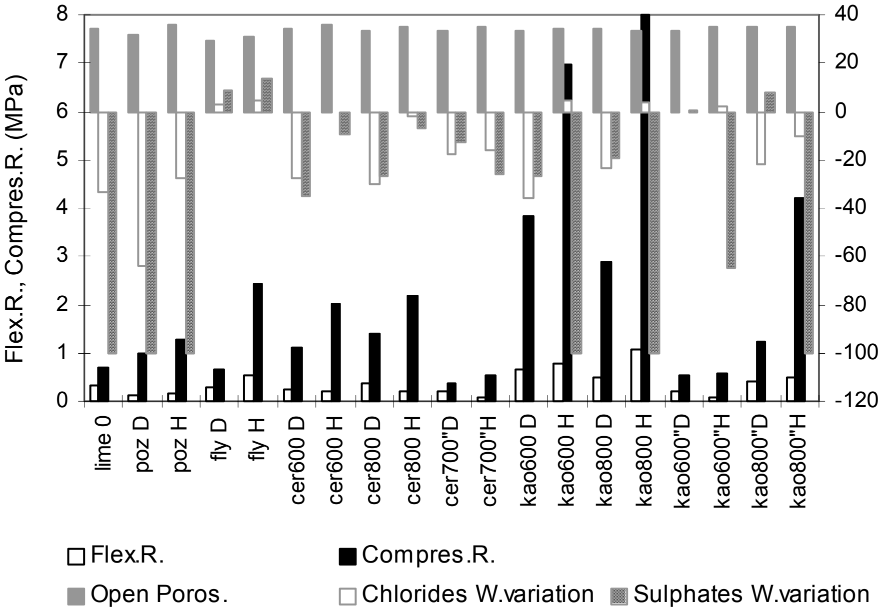

Fig. 7 – Open porosity, mechanical, chloride and sulphates resistance of mortars

The lower values of open porosity are presented by the mortars with fly-ash. The mortars with each pozzolanic component, cured under humid conditions, currently present a higher value of open porosity than the similar mortar submitted to dry cure. Hypothetically these differences can be justified by differences on pore size distribution. A possibility is that when the water leaves the pores of mortars under humid cure, those mortars are sufficiently hard so the retraction is not high and the pores stabilize with the volume they had when partially full of water. Simultaneously with a longer pozzolanic reaction development (when humid cure conditions are present), less quantity of calcium oxide could possibly remain free so that a lower volume of the pores will be occupied with calcium carbonate.

As expected, the mechanical characteristics are generally improved with the use of pozzolanic components (except for the cases of clay material fired at low temperature for a short period – **cer700”** and **kao600”**) and the values are sensible to the introduction of humid cure conditions.

The weight variation by chlorides action on the pozzolanic mortars is lower than for the control lime mortar (except for the **poz D** mortar), what shows that those components contribute to the improvement of resistance to chlorides of lime based mortars. It is also clear that the humid cure conditions contribute to the improvement of resistance to chlorides of mortar with the same pozzolanic components. But the improvement of chlorides resistance is not always associated with the mechanical resistances, as can be seen, for instance, in the cases of mortars **fly D**, **cer700”D** and **H**, **kao600”D** and **H**. That can possibly be explained by different pore size distribution of the mortars, which allow the formation and dissolution of halite crystals in the volume of the pore, without damages. Simultaneously it could be possible to admit the formation of Friedel´s salt, which would consume chloride ions by sticking them to the alumina of the pozzolanic components

In what concerns the sulphates action, it can be emphasized the special good behaviour of the mortars containing fly-ash, the efficient performance of all the mortars with ceramic fired material and the differentiated comportment of the mortars containing fired kaolin (presenting especially good performances for the cases of mortars under dry cure with low fired material and inefficient comportment in the cases of humid cured mortars with high fired material). In accordance with the results of pozzolanic reactivity and the observed development of CSH, the fired kaolin seemed to be the more reactive, inducing a stronger development of hydraulic compounds. Under sulphate attack, this calcium silicate hydrates CSH (and eventually other calcium aluminates hydrates CAH), can form sulpho calcium silicate hydrates (and sulpho calcium aluminates hydrates), which are very expansive and destructive.

By comparison between the weight variation by chlorides and by sulphates actions, it can be observed that a mortar that present a good resistance to one of these attacks does not necessarily have an efficient resistance to the other (as the cases of mortars with fired kaolin under humid cure – **kao800 H**, **kao600 H**, **kao800”H** and **kao600”H**), what confirms that chlorides and sulphates produce different attacks on the analyzed mortars. The performances of mortars to the attack of salts may be increased with high mechanical resistances (for lime based mortars) while other conditions like pore size distribution (for the case of chlorides) and the hydraulic compounds formed (for the case of sulphates) can present a more important role.

4. Conclusions

The resistance to chlorides and sulphates of hydrated lime and pozzolanic components mortars emphasizes the fact that the mechanical resistances can only partially contribute to an efficient performance of this kind of mortars. One of the reasons can be the relatively low mechanical strength of mortars compatible with historic buildings.

In what concerns the chlorides resistance, an important role can possibly be played by the pore size distribution of the material and the probable chloride ions consumed by Friedel´s salt formation.

Regarding to the sulphates resistance, a compromise must be achieve between the hydraulicity of the mortars (in terms of CSH and CAH formation) so that the sulpho calcium silicates and aluminates hydrates formation could be controlled.

The addition of pozzolanic components to hydrated lime mortars can improve the soluble salts resistance of these mortars. Different pozzolanic components can be used, some of them industrial by-products used directly or after simple and low cost preparation. A great importance should be given to the cure conditions of the mortars.

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