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Effect of the Mineralogical Composition of Limestone on the Properties of Mortars

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Abstract

Limestone has been used as a partial substitute for cement, due to its beneficial effect on mechanical properties of mortars and concretes. In the present research, we studied the effect of the mineralogical composition in mortars produced from limestone samples collected in different areas of Mozambique, using two cement types (Portland cement 32.5N and 42.5N). Additions of 10 to 25% limestone gave, in general and for the 32.5N cement, good results of the compressive strength for all limestone samples, while for the 42.5N only the Massinga samples performed well. Effect of the limestone additions on the flexural strength showed a beneficial effect for all samples and at all compositions studied, when using the 42.5N cement, while for the 32.5N cement only additions of 10% limestone gave values of the flexural strength higher than the reference material, with the exception of the Magude samples.

Keywords

Mortars, Concrete, Limestone, Filler

1. Introduction

The use of limestone as partial replacement for cement and fine aggregates in concretes and mortars is receiving increasing attention in recent years. Its use contributes for cost savings through replacement of cement or sand by a product of the limestone extraction industry, and for reduction of the environmental pollution through elimination of dust disposal and reduction of CO_2 emissions associated with cement production [1]-[4].

Limestone fines have been used as the only substitute or in combination with other materials with a potential pozzolanic activity like blast-furnace slags and ashes from agriculture by-products [5]-[8]. Ashes become a rele-

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vant pozzolanic material when processed under conditions where a significant amount of amorphous silica is developed [4]. These materials present a better reactivity with cement components and develop normally a better strength than the effect observed with limestone additions, giving values of the compressive strength more similar to the values obtained for the conventional material, even for higher substitution of cement [9] [10].

It has a physical effect (filler effect) and also a chemical contribution in the improvement of the properties of mortars and concretes. It reacts with tri-calcium aluminate in cement to form calcium carbo-aluminate; promotes early hydration of cement and interacts with aluminate formed during hydration, leading to a decrease of porosity and increase of strength of concrete, within certain amounts of limestone [1] [10] [11].

Menadi *et al.* [2] worked with 4 different cements to prepare samples from the conventional material (without replacement of sand by limestone) and samples where sand was replaced by 15% limestone and registered a decrease in compressive strength for all cement types. Menéndez *et al.* [5] reported an increase of the compressive strength at earlier curing ages (1, 7 and 14 days) and comparable values by 28 days curing age, in compositions where 10% Portland cement had been replaced by limestone. When the amount of cement replaced was increased to 20% compressive strength reduced at all curing ages. Limestone showed, at same amounts and at curing ages of 1 to 28 days, a better effect than the blast-furnace slag with a high amount of SiO_2, normally present in amorphous form, while blast-furnace slag seemed to develop a better strength at higher curing ages (90 days).

Meddah *et al.* [1] worked with contents of limestone varying from 15 to 45% and registered a decrease in the entire interval, even at the different water to cement ratios they worked on. Lollini *et al.* [12] showed a significant increase of properties of concrete, but their results shall be discussed carefully since they used a synthetic binder that might have a significant contribution in the improved properties, contrary to the work where no synthetic binder had been used.

Bizzozero and Scrivener [11] studied the effect of the replacement of 20% cement by 20% limestone, on one side, and 20% quartz, on the other side, in low and high calcium sulphate environments. Mortars with limestone show, in low calcium sulphate environments, results of the compressive strength are more similar to the conventional mortar (without substitution) when compared to mortars with quartz, at different curing ages. In high calcium sulphate environments higher results of the compressive strength are obtained for conventional mortar and mortars with substitution by quartz and limestone, but results for both substituents are lower than the ones obtained with conventional mortar, with quartz and limestone mortars producing comparable results.

In a long term, limestone additions to materials used in high sulphate environments lead to formation of gypsum by reaction with the sulphate and the resulting decrease in compressive strength [3]. The role of sulphate is not consensually described. Ghrici *et al.* [13] report a beneficial effect of limestone on the improvement of sulfuric acid resistance. They also show a different effect of mortars exposed to sulphate introduced in different forms (5% Na_2SO_4 and 5% $MgSO_4$), with Na_2SO_4 causing higher expansion and a more detrimental effect on the mechanical resistance. This seems to be the case in an initial phase [3] but with time material develop expansion and cracking, with the consequent effect on strength. According to Chang *et al.* [14] limestone reduces acid concentration near the surface of the material and the rate of degradation of concrete subjected to acid attack, however mechanisms of degradation is not yet fully understood.

In the present study we aimed to study the effect of the mineralogical composition in mortar properties by replacing cement by limestone samples collected in different areas of Mozambique (Magude, Massinga and Salmanga). In the production of mortars we used two cement types (Portland cement 32.5N and Portland cement 42.5N) in order to compare the effect of the two cement types on properties of mortars.

2. Materials and Methods

After collection, samples were crushed, milled, and sieved through a 150 µm and dried before preparation of samples for the technological tests. Coarse aggregates, obtained after crushing, were used to test attack by sodium sulphate and potential reactivity of the limestone samples, based on the norm ASTM C 289-1971 [15]. The fine samples where then submitted to a chemical and mineralogical composition, by XRF and XRD respectively, at XRD Analytical and Consulting CC in Pretoria, South Africa.

For preparation of concrete samples for the technological tests (according to the norms ASTM 91977; NM NP EN 197-1:2000 and NBR 9778 (1987)) [16]-[18], cement was partially replaced by amounts of the different limestone powders in the amounts shown in **Table 1**.

Table 1. Composition of samples used in technological tests.

Sample	Amountofcement (g)	Amountoflimestone		Sand (g)	Water (mL)
		(%)	(g)		
Reference	450	0	0	1350	225
F10	405	10	45		
F15	382.5	15	67.5		
F20	360	20	90		
F25	337.5	25	112.5		
F30	315	30	135		

Samples prepared using the six limestone samples tested in this study (labelled MG1, MG2, SL1, SL2, MS1 and MS2) were then prepared by weighing/measuring the respective amounts of cement, limestone, sand and water, according to the proportions given in **Table 1**. These samples were prepared with two types of Portland cement namely the 32.5N and the 42.5N cement.

After weighing the right amount of each component, these were inserted in a mechanical mixer where they were thoroughly mixed, starting with a low velocity (140 ± 5 r.p.m.) which was increased after one minute to a mixing velocity of 285 ± 10 r.p.m.

Prepared mass was then poured into prismatic moulds with 160 × 40 × 40 mm^3, compacted and maintained on a conditioning chamber for 24 hours, before demoulding (see norm NM NP EN 197-1:2000) [17]. After demoulding, specimens were submitting to curing in water tanks, until curing age was reached, and then submitted to the mechanical tests (flexural strength, compressive strength and water absorption test).

Results of the flexural and compressive strength of the samples with limestone were statistically compared against conventional mortars to verify existence or not of significant differences. These results were then combined with results of the attack by sodium sulphate solution and potential reactivity to decide about applicability of the different compositions.

3. Results and Discussion

In this study we used 6 limestone samples collected in Magude (MG1 and MG2), Massinga (MS1 and MS2) and Salamanga (SL1 and SL2). The Salamanga samples are presently used for cement production by Cimentos de Moçambique, the main cement company in Mozambique, while the samples from Massinga are used in concrete production and the Magude samples have been used for paving works. **Table 2** shows the chemical composition of the samples while **Table 3** presents the results of the semi-quantitative mineralogical composition. Massinga and Salamanga samples show predominantly calcite while the Magude samples present a high amount of dolomite and quartz in its composition.

Results of the effect of the partial replacement of cement by limestone in concrete masses on the mechanical properties of the mortars are presented in **Table 4** and **Table 5** for the samples prepared with the 32.5N and the 42.4N cement respectively.

For a better comparison, these results are graphically presented in **Figures 1-6**. The Massinga samples (MS1 and MS2), with the higher calcite contents show the best performance, particularly at 10 and 20% replacement.

Results of the attack by the sodium sulphate solution for the Massinga samples (MS1 and MS2) showed values of 8.3% and 10.97% respectively, values below the maximum limit allowed according to the norm ASTM C88 (1976). Magude (MG1 and MG2) and Salamanga (SL1 and SL2) samples showed results above the maximum limit. Results of the potential reactivity against alkalis gave for the Massinga samples good results, thus supporting its potential applicability as aggregate in concrete masses. Massinga samples were the only ones tested for potential reactivity, based on the bad results of the sulphate attack for Magude and Salamanga samples.

Results of the flexural strength show, in general, lower values for the 32.5N cement and higher values for the 42.5N cement. Results with the 32.5N cement are more uniform, while the results obtained with the 42.5N cement are higher for the Massinga samples.

Table 2. Chemical composition of studied samples.

Component	Contents in %							
	Limestone samples						Cement	
	MG1	MG2	SL1	SL2	MS1	MS2	32.5N	42.5N
CaO	28.99	25.97	49.47	48.48	54.68	54.84	61.19	57.76
SiO_2	26.79	22.54	5.00	5.61	1.98	2.85	13.90	19.59
Al_2O_3	5.33	4.21	1.14	1.05	0.70	1.02	2.80	6,91
Fe_2O_3	2.19	2.00	0.77	3.65	0.35	0.55	3.10	2.67
MgO	4.49	11.47	0.63	0.67	0.29	0.28	0.93	1.84
SO_3	0.04	0.14	0.04	0.02	<0.01	0.01	3.28	4.30
Na_2O	0.36	0.29	0.18	0.01	<0.01	<0.01	0.02	0.03
K_2O	0.83	0.53	0.40	0.56	0.18	0.18	0.67	0.59
LoI	28.75	32.99	40.29	39.27	41.98	41.65	12.06	5.27

Table 3. Mineralogical composition of the samples.

Phase	Contents in %					
	MG1	MG2	SL1	SL2	MS1	MS2
Calcite	33.00	3.86	95.71	94.58	98.24	98.70
Montmorilonite	1.74	0.31	-	-	-	-
Quartz	11.82	8.95	4.29	5.42	1.16	1.30
Dolomite	43.60	80.06	-	-	-	-

Table 4. Average results of flexural strength, compressive strength and water absorption after 28 days (samples prepared with the 32.5N cement).

Property	Content of Limestone (%)	Samples						
		Reference	MG1	MG2	SL1	SL2	MS1	MS2
Flexuralstrength (**MPa**)	10	6.37	5.64	6.23	6.62	6.64	6.47	6.66
	20	6.37	5.50	5.80	5.50	6.02	5.57	6.07
	25	6.37	4.95	5.31	5.15	5.76	5.20	5.83
	30	6.37	4.45	4.35	4.81	4.93	4.85	5.22
Compressivestrength (**MPa**)	10	32.73	32.54	32.76	32.73	32.79	32.80	33.46
	20	32.73	31.90	32.48	32.48	32.50	32.58	32.56
	25	32.73	31.38	31.94	31.58	31.98	32.10	32.42
	30	32.73	26.78	30.80	30.80	31.32	31.20	31.47
Waterabsorption (%)	10	3.44	3.73	3.52	3.44	4.02	5.02	5.27
	20	3.44	4.00	3.62	4.03	4.17	5.27	5.29
	25	3.44	4.04	3.87	4.10	4.22	5.89	5.71
	30	3.44	4.43	4.16	4.23	4.55	5.99	5.90

Table 5. Average results of flexural strength, compressive strength and water absorption after 28 days (samples prepared with the 42.4N cement).

Property	Content of Limestone (%)	Samples						
		Reference	MG1	MG2	SL1	SL2	MS1	MS2
Flexural strength (**MPa**)	10	7.98	9.64	10.49	9.83	10.57	12.18	12.47
	15	7.98	8.61	10.90	9.22	10.20	11.51	11.70
	20	7.98	9.31	9.35	9.65	9.70	11.40	11.45
	25	7.98	8.40	8.86	9.13	9.17	11.20	11.28
Compressive strength (**MPa**)	10	39.00	30.18	33.15	35.79	38.55	36.97	43.90
	15	39.00	26.88	32.57	32.31	35.28	33.46	42.73
	20	39.00	24.30	30.78	29.91	31.73	34.63	40.06
	25	39.00	22.38	24.99	26.13	26.20	34.63	39.49
Water absorption (%)	10	3.53	5.17	3.52	3.44	4.02	5.02	5.27
	15	3.53	5.13	3.62	4.03	4.17	5.27	5.29
	20	3.53	5.62	3.87	4.10	4.22	5.89	5.71
	25	3.53	5.61	4.16	4.23	4.55	5.99	5.90

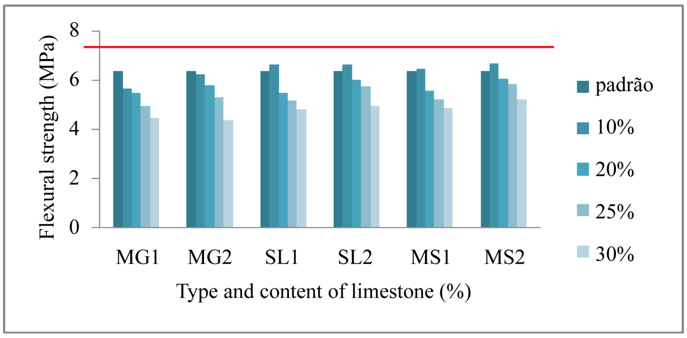

Figure 1. Flexural strength after 28 days curing age (specimens prepared with the 32.5N cement).

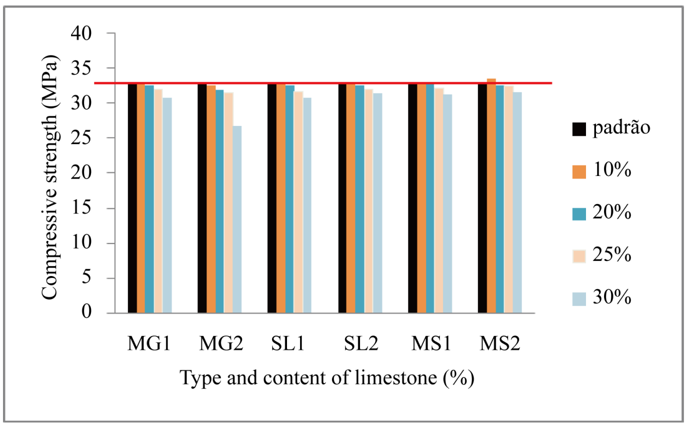

Figure 2. Compressive strength after 28 days curing age (specimens prepared with the 32.5N cement).

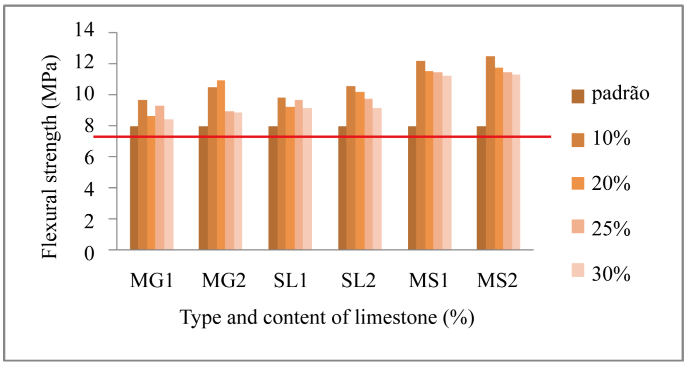

Figure 3. Flexural strength after 28 days curing age (specimens prepared with the 42.5N cement).

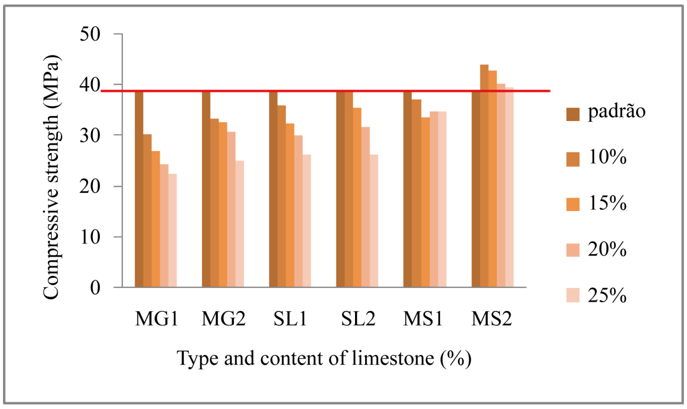

Figure 4. Compressive strength after 28 days curing age (specimens prepared with the 42.5N cement).

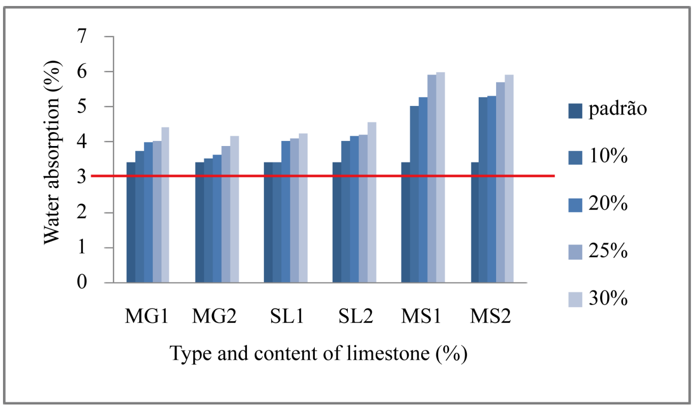

Figure 5. Water absorption after 28 days curing age (specimens prepared with the 32.5N cement).

Results of the compressive strength, for the 32.5N cement, show a more uniform behaviour, particularly for the Salamanga (SL1 and SL2) and Massinga (MS1 and MS2) samples, even for additions of limestone up to 25% - 30%. Values are slightly lower when compared with the reference material. Values obtained with the 42.5N cement with the Magude (MG1 and MG2) and Salamanga (SL1 and SL2) samples are significantly lower than the ones obtained with the reference material. The Massinga samples show the best results, particularly the MS2 samples, which show results of the compressive strength higher that the values obtained with the reference material for all contents of limestone (10, 15, 20 and 25%), with an increase of the compressive strength of 10%

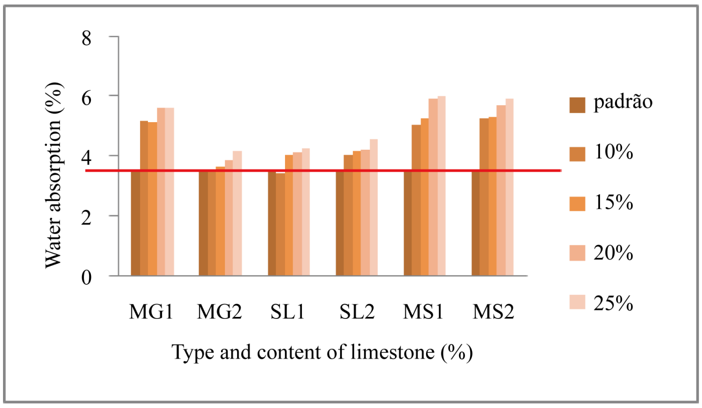

Figure 6. Water absorption after 28 days curing age (specimens prepared with the 42.5N cement).

- 12% for additions of limestone of 10 to 15%.

The water absorption experiments gave values higher than the values of the reference composition, with the samples MG2 and SL1 giving results with the lowest deviations, while samples MS1 and MS2, the samples with the best compressive and flexural strength, show the highest values of the water absorption (**Figure 5** and **Figure 6**).

In general, additions of 10 to 25% gave, for the 32.5N cement, good results of the compressive strength for all limestone samples, while for the 42.5N only the MS2 sample performed well. Effect of the limestone additions on the flexural strength show a beneficial effect for all samples and at all compositions studied (10 to 30% limestone addition), when using the 42.5N cement, while for the 32.5N cement only additions of 10% limestone gave values of the flexural strength higher than the ones obtained with the reference material, with the exception of the Magude samples (MG1 and MG2).

Results obtained with the 42.5N cement for the Massinga samples are more similar with the results obtained by Knop *et al.* [10], Bizzozero and Scrivener [11] and Menéndez *et al.* [5], authors that used a 42.5N cement type. The decrease of the compressive strength in the entire interval, reported by Meddah *et al.* [1], contrary to the results of this study and the results obtained by Knop *et al.* [10], Bizzozero and Scrivener [11] and Menéndez *et al.* [5], may be explained by the fact that Meddah *et al.* [1] worked with limestone contents higher than 15%, highest beneficial value reported by the other authors.

Calcite limestone samples show, in general, better results, when compared to the dolomitic ones, but the effect of calcite limestone cannot be assessed based only on the mineralogical composition, since Salamanga and Massinga limestone samples show nearly similar calcite contents with 95.71 and 94.58% calcite on Salamanga samples and 98.24 and 98.70% on Massinga samples (see **Table 2**). CaO content goes from nearly 49% in Salamanga samples to 54% in the Massinga samples (see **Table 1**). The expected improvement of the compressive strength achieved by replacement of cement by dolomite limestone reported by Mikhailova *et al.* [19] was contrary to the results obtained in this study.

Statistical treatment of the results of the flexural and the compressive strength, aimed to test eventual differences among the results, showed for the samples prepared with the 32.5N cement good results, except for the MG1 limestone samples. No significant differences were observed for the compressive strength results of the samples with 10% limestone addition, in comparison with the reference concrete. The flexural strength results for the 10% replacement were all statistical different but results obtained are higher than the ones obtained for the reference concrete mass. All other results (flexural and compressive strength) obtained with the samples with more than 10% were different and lower than the conventional concrete sample.

Statistical treatment of the results (flexural and compressive strength) of the specimens prepared with the 42.4N cement were all significantly different from the ones obtained with the reference concrete, but fortunately flexural strength results of the samples prepared with all limestone samples (MG1, MG2, SL1, SL2, MS1 and MS2) for all compositions (10, 15, 20 and 25% limestone) are higher than flexural strength of the reference sample. On the other side, comparison of the compressive strength gave good results only for the MS2 limestone: Although statistical different, MS2 gave for all compositions (10, 15, 20 and 25% limestone) values of the compressive strength above the values obtained for the reference material, thus confirming its potential to replace cement in the above mentioned contents.

4. Conclusions

Results presented show a beneficial effect on the mechanical properties of mortars were cement has been partially replaced by limestone, particularly when using calcite limestones. The Massinga samples with reference MS2 showed the best results in the mechanical properties of mortars as well as in the potential reactivity against alkalis.

Although results presented bring evidence of the beneficial effect of limestone additions, in general, at contents not higher than 15% limestone, further research is needed to better clarify the effect of other variables, like e.g. the water to cement ratio. Since some properties change on a long-term, some properties of the materials (e.g., the decrease of the compressive strength in high sulphate environments reported by Pipilikaki *et al*. [3]) must be monitored over the 28 days curing age normally used as reference curing age.

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