EFFECTS OF ADDITIVES ON GYPSUM SLURRY BEHAVIOUR

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Abstract

The implementation of this study is based on methodology, exploring opportunities for adding of inorganic mineral additives in suspension of β-hemihydrate form obtained from desulfo-gypsum. The main purpose as to study the changes in gypsum slurry behaviour by incorporating three rates (5%, 15% and 25%) of Na-feldspar, dolomite and waste marble powder as substitutions of hemihydrate material. The research framework includes tests based on standards for gypsum based building materials. These incorporates analyzes of physical and chemical properties of the raw materials, examination of prepared gypsum slurries and tests on the set composite samples. All types of mineral additives included at gypsum mixture recipe have different morphological characteristics and physicochemical properties, which impact in diverse ways of prepared gypsum bodies. The results obtained show that the difference in structure, origin and chemical composition of minerals additives determines the behaviour of prepared gypsum slurries and the properties of set gypsum bodies.

Key words: *calcium sulphate, mineral additive, efficiency*

INTRODUCTION

Sustainable building materials creation is based on the positive life cycle assessment concept. New construction materials are designed to meet the sustainable development policy in aspect of whole life cycle of the products in a broader aspect, including efficient natural resources usage. It is a prerequisite for energy efficiency increasing, which in turn leads to decreasing industrial environmental impacts.

One of the most prospective industrial minerals used in green construction materials manufacturing is calcium sulfate dihydrate. From raw mineral to high-end composite $CaSO_4.2H_2O$ passes through a number of energy-intensive processes which have their own footprint on the environment. There are investigated various efforts underway to improve gypsum products life cycle and make it suitable as an eco-friendly material in terms of binder amount decreasing. The most practices in regard to suitable binder substitutes usage are directed to industrial waste materials application (Rodriguez, et. al., 2013; Yazici, 2007) as blast furnace slag (Mridul et. al., 2014; Zhong et. al., 2012) and silica fume (Demir et. al., 2008; Rivera et. al, 2012) even if the main raw material is a synthetic gypsum. There are many studies on new plaster material recipes containing various mineral additives as perlite, metakaolin and lime (Morsy et. al., 2012; Hua et. al., 2010; Shen et. al., 2007; Vimmrova et. al, 2014; Fraire-Luna et al, 2006) which aim is to improve materials properties and to replace part of hemihydrate amount.

This paper focuses on studying the benefits and limitations of three type mineral aggregates added to gypsum mixture as hemihydrate substituents: waste marble powder, sodium feldspar and dolomite.

1. EXPERIMENTAL

1.1. Materials and Methods

Experiments were conducted with three mineral aggregates added to β-hemihydrate of desulfurization gypsum: sodium feldspar, marble powder and dolomite. Materials chemical composition is presented in Table 1. Figure 1 illustrates the particle size distribution of calcium sulfate and mineral additives. This study is carried out in accordance to the standards of gypsum binders and gypsum plasters (EN 13279), gypsum boards with fibrous reinforcement (EN 15283) and gypsum plasterboards (EN 520). All experiments were conducted under laboratory conditions.

1.2. Sample preparation

Preliminary tests of slump-flow, setting time, and water-hemihydrate ratio were conducted to be analyzed the basic properties of gypsum-water suspension and referred to gypsum-additive pastes parameters. To obtained comparable results, all samples were prepared in standard water-binder ratio of 0.70. Three samples were tested for each experiment and average result was calculated. To be examined the mechanical behavior gypsum prismatic bodies of 40x40x160 mm were prepared (according to EN 13279). Specimens prepared for fire resistance test (45x12.5x300mm) were examined in accordance to EN 520. All prepared set plaster bodies were cured in ambient environment temperature of 23°C in relative humidity of 50% for 7 days and dried to constant mass.

Table 1 Mineral additives chemical composition, (%)

(Sodium feldspar)		Dolomite		Marble powder	
Al_2O_3	min. 19.00	MgO	min. 20.0	CaO	54-55
Fe_2O_3	max. 0.50	CaO	min. 30.0	MgO	0.5-1
TiO_2	max. 0.45	Al_2O_3	max. 0.4	Mineralogical composition:	
$Na_2O + K_2O$	min. 9.50	SiO_2	max. 1.0	Dolomite	2
SiO_2	max. 70.00	Fe_2O_3	max. 0.15	Calcite	96
CaO + MgO	max. 3.00			Quartz	2
Loss of ignition	max. 0.50				

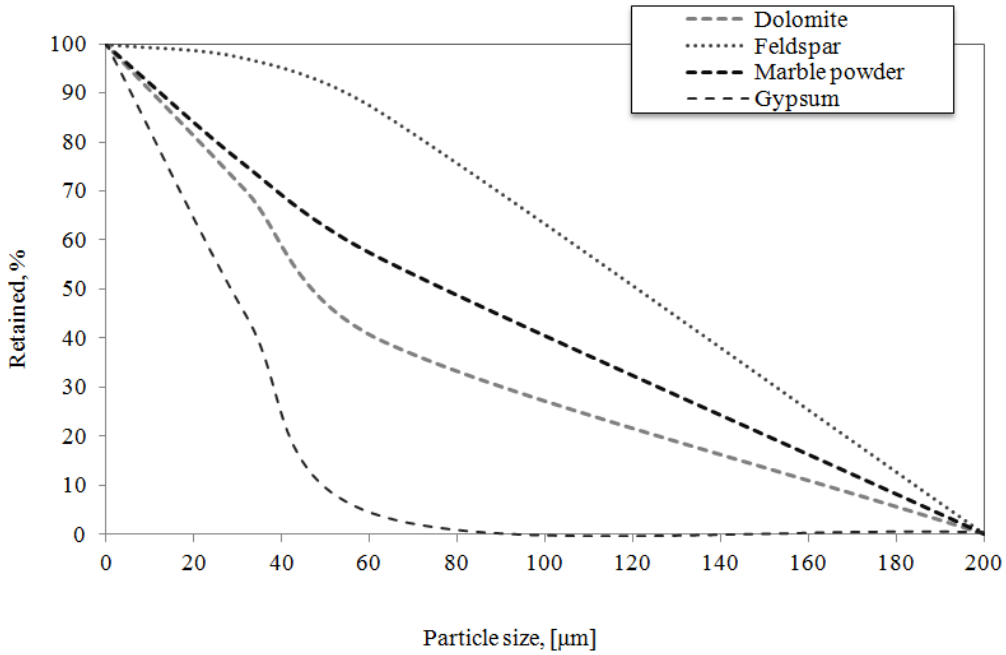


Figure 1 Raw materials particle size distribution

Table 2 Calcium sulfate hemihydrates main parameters

Analysis	Type	Unit	Results
Density	Bulk density	g/cm^3	0,758
	Tapped density	g/cm^3	1,024
Fineness (Blaine)		cm^2/g	5020
pH			6.34
water-binder ratio			0.67
Combined water		%	6,71
	$CaSO_4$	%	0,2
Phase content	$CaSO_4.0.5H_2O$	%	86.82
	$CaSO_4$ (s)	%	0,24

2. RESULTS AND DISCUSSIONS

2.1. Mixture elaboration

Several tests on gypsum-additive mixture with different percentage of mineral fillers were conducted. Suspension flowability and setting times of the designed mixtures were tested. The three mineral additives- dolomite, feldspar and waste marble powder were added in three percentages by plaster weight in increments of 10%. Slump flow test was determined by Southard viscometer and setting time test was conducted by the knife method. Setting time test results are listed in Table 3 and slurry flowability is illustrated on Figure 2. Gypsum hemihydrate-water samples without mineral fillers addition (standard samples) were prepared for reference purposes to be comparable the results obtained with the rest of tested samples.

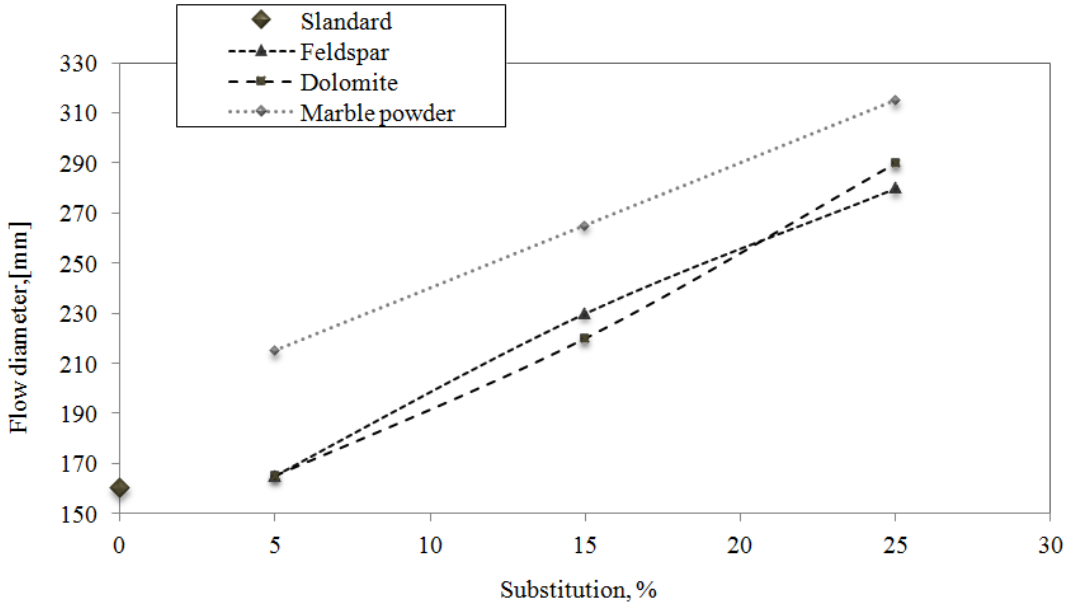


Figure 2 Suspension flowability results with different percent of substitution material

Table 3 Suspension setting time, (min:sec)

Standard		**Substitution**	**Feldspar**		**Dolomite**		**Marble powder**	
initial	final		initial	final	initial	final	initial	final
01:40	04:10	5%	01:50	04:10	02:00	04:25	01:50	04:15
		15%	02:00	04:20	02:05	04:20	02:00	05:05
		25%	02:10	05:20	02:10	05:20	02:10	05:50

This experimental part investigates gypsum suspension flowability after mineral fillers addition. Based on the results obtained it was observed a substantial increase of slurry fluidity when mineral fillers added. The addition of 5% feldspar and dolomite slightly changes flow diameter, but 5% marble powder addition increased it with 34%. Hemihydrate replacement by 15% fillers has increasing effect on the flow diameter with feldspar- 44%, less change occurred in dolomite addition only 38%, but suspension viscosity growing with marble powder incorporation by approximately 66%. By adding the highest percentage mineral component, there was an almost double increasing flowability of the composite mixture with the addition of 25% marble powder, and the equal amount dolomite and feldspar addition results on diameter growing with 75-80%. The main reason for the viscosity increase is the reduced hemihydrates content in the mixture. Because the additives behave as inert and do not react with water, a high amount of free water stays in the slurry unused. A second reason for the viscosity growth is the slight longer setting times of the mixture. As it could be seen from the results presented in Table 3, setting time could be extended by mineral fillers addition. Time increases proportionally with respect to mineral additive ratio. Best results were achieved with 25% filler addition, as for all the initial setting times the increase was with 0:30 sec., while the longest setting final was achieved by marble powder addition, extended with 01:40 min. Samples prepared with feldspar and dolomite setting final was equal for both samples with 01:10 min. longer than that standard sample. Normally increased fluidity and setting time retarding is a prerequisite for reducing the quantity of chemical modifiers used in composites production. On the other hand should be noted that the setting time control is extremely important especially in the production of plasters and mortars.

2.2 Mechanical characteristics

Strength-deformation characteristics were studied on set gypsum-additive prismatic bodies, pre-dried and conditioned in a desiccator. The prisms were subjected to a three point-loading test, according to the standard EN 13279. This method was used to determine the flexural strength of gypsum-additive prisms. The resulting half prisms were subjected to uniaxial compressive strength determination. Results illustrated on Figure 3 and Figure 4 shows that the samples demolition resistance decreases by increasing the amount of mineral addition. Plaster samples sustained gradual strength losses down to 2,77N/mm^2 due to increasing amount of dolomite in 25% of binder weight. Reference sample containing pure gypsum registering flexural strength values of 4.29 N/mm^2, and the 15% sodium feldspar addition sample strength obtained was 4.11 N/mm^2. Observed diminishing of flexural strength was due to the different proportions of calcium sulfate and additive. Strength results of 15% mineral addition for all three types of fillers were in range 3-4.1 N/mm^2, as the lower results were observed when added marble powder. All tested plaster bodies showed strength deterioration than the standard sample.

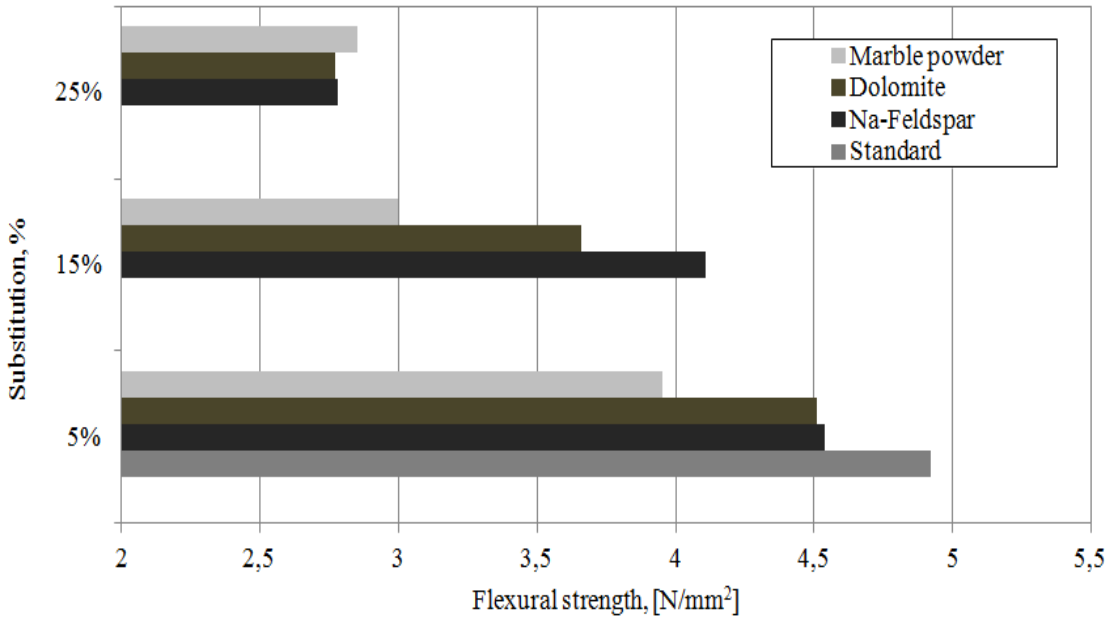


Figure 3 Flexural strength test results determined by Zwick Roell z010 device

The effects of inert material addition on the compression durability in terms of the stress–strain relationships for tested specimens illustrated on Figure 4 clearly shows that in most cases the addition of mineral filler deteriorates the compressive strength. Commonly, when additive is mixed with hemihydrate there is not enough strong bonding between them that could provide composite matrix improvement. The compressive strength of gypsum-inert material hardened samples was lower than gypsum reference sample at the entire studied range of filler concentrations. The general trend was that the samples compressive strength decreases with increases of additives content. Samples made with 25% marble powder had the highest strength among all samples in 25% addition. 15% feldspar addition decreases strength with almost 33% to 13.5 N/mm^2, and marble powder decreases strength with 21% to 15.9 N/mm^2.

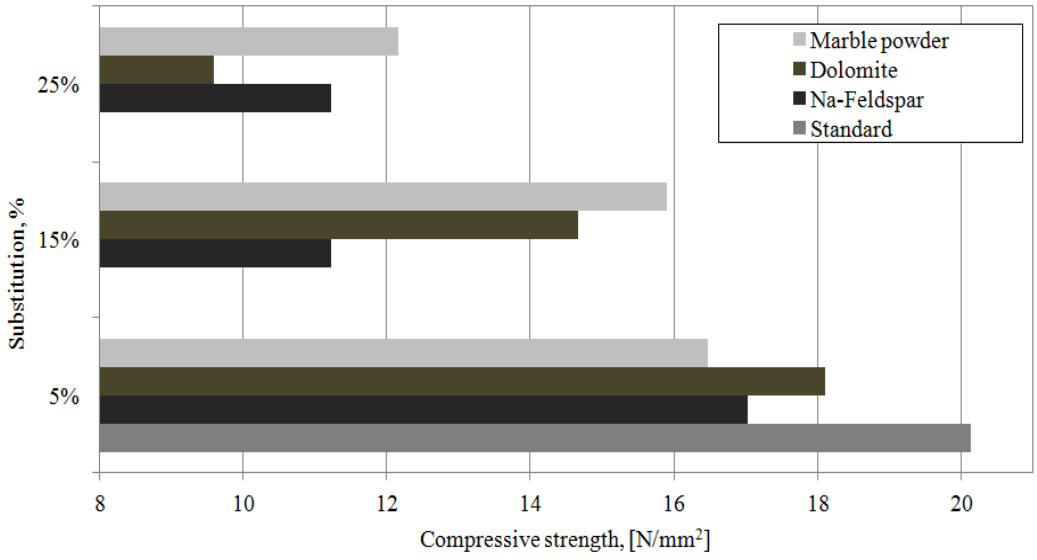


Figure 4 Compressive strength results

2.3 Core cohesion

It was studied fire resistance of plaster specimens in three main ratios of inert materials addition (5%; 15%; 25%). Prefabricated molds were developed to simulate standard fire-resistant samples 45 x 12.5 x 300 mm in accordance the EN 520 and exposed to Meker-Fisher burners in temperature range of 1000-1150^{0}C. When 5% of inert materials added, similar failure values in time resistance was registered for all tested samples. While the fire-resistance time of referent mixture was 19 sec., the resistance of mixture containing 25% of marble powder increases to 81 sec. for the marble powder, 72sec. for dolomite and 45 sec. for Na-feldspar, as shown in Figure 5.

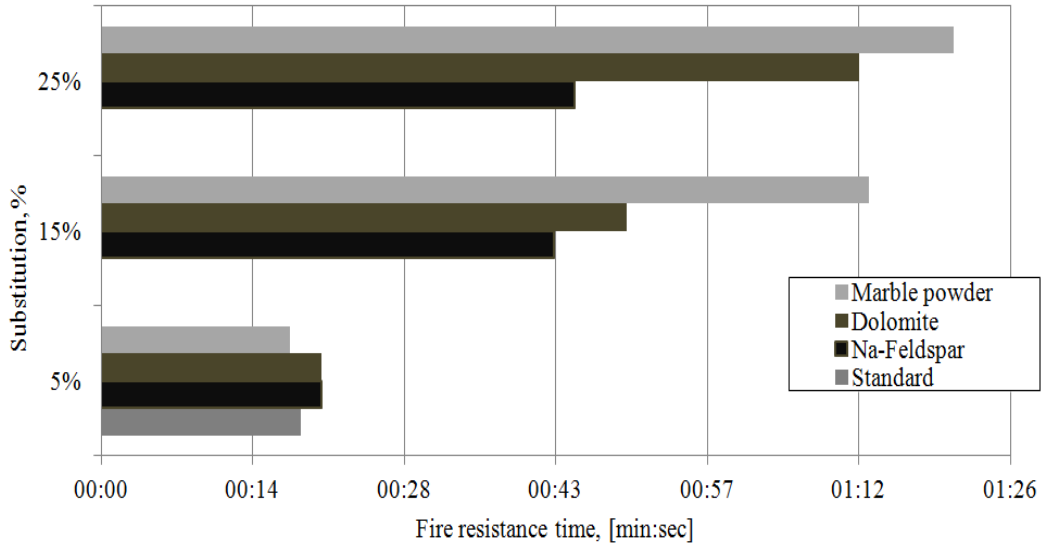


Figure 5 Core cohesion test results

2.4 Water absorption

It was found that all assayed mineral fillers could maintain or slightly increase water absorption of the hardened gypsum samples. Adding of 5% feldspar increasing the absorption with 2%, dolomite and marble fillers retains water absorption as reference sample. Feldspar influence was maintained even with the addition of another 10% filler material, so in 15% feldspar content the water absorption of plaster bodies retained with 2.7% higher than the standard sample. The absorption of dolomite and marble powder composites in 15% addition was equal to both tested specimens about 3% higher than reference sample result. The trend in water absorption in the highest rates dolomite and marble addition results in increase of only 4%. Water absorption peak was obtained after 25% feldspar addition which was 5.5% higher than the reference sample.

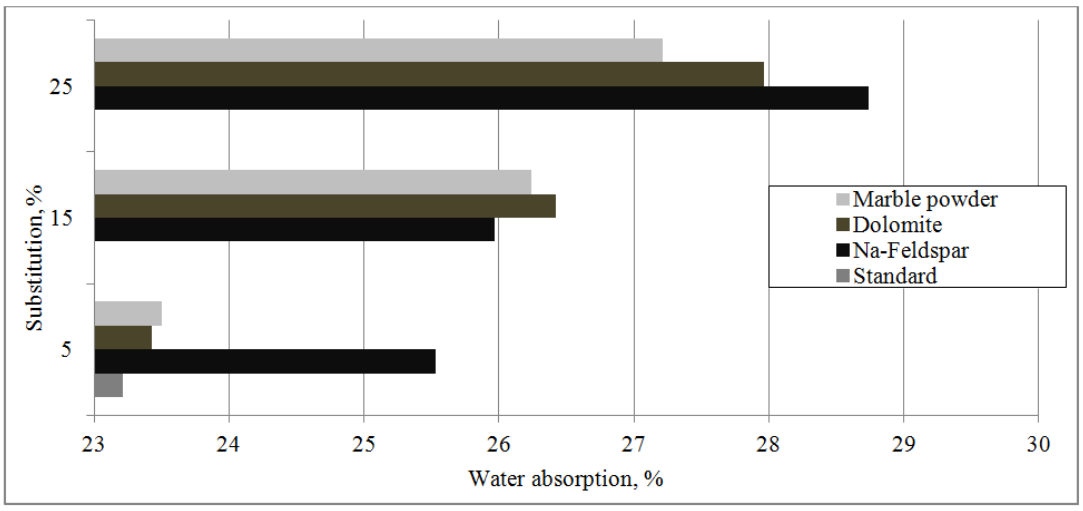


Figure 6 Water absorption test results

3. CONCLUSIONS

An improved performance in fresh state behavior and fire resistance properties for traditional gypsum based materials can be achieved by replacements of 15–25% hemihydrate by feldspar, dolomite or waste marble powder. From the results obtained it can be concluded that to increase fluidity of the composite suspension it is useful mineral fillers addition, as the highest results were obtained by 25% marble powder incorporation. The set gypsum-additive bodies show good fire resistance, especially when 25% of marble powder is added. The increased amount of mineral fillers do not changes significantly the setting times of the slurry. From the three inert materials studied and compared best results were observed with 15% to 25% marble powder addition, so its usage for plaster based products is favorable. Although, the overall mechanical strength of the specimens prepared decreases, the best strength properties shows samples prepared with marble powder. The compressive strength for pastes with 25% inert materials is lower than this with pure gypsum binder. Additional adaption of water-gypsum ratio can improve the strength results. The water absorption increases to maximum 5.5% than reference sample.

In addition, the effective use of waste marble powder, and other inert mineral additives in combination with waste gypsum in building materials production, contributes to developing a sustainable establishing environment.

REFERENCES

Demir, I., Baspinar, S. M., 2008, ‘Effect of silica fume and expanded perlite addition on the technical properties of the fly ash–lime–gypsum mixture’, Construction and Building Materials, no. 22, pp.1299–1304

Fraire-Luna, P.E., Garcia, E. I. J., Gorokhovsky, A., 2006, ‘Composite systems fluorgypsum – blastfurnance slag–metakaolin, strength and microstructures’, Cement and Concrete Research, no.36, pp.1048–1055

Hua, M., Wang, B., Chen, L., Wang, Y., Quynh, M. V., He, B., Li, X., 2010, ‘Verification of lime and water glass stabilized FGD gypsum as road sub-base’, Fuel, no. 89, pp.1812–1817

Morsy, S. M., Alsayed, H. S., Salloum, A. Y., 2012, ‘Development of eco-friendly binder using metakaolin-fly ash–lime-anhydrous gypsum’, Construction and Building Materials, no.35, pp.772–777

Mridul Garg, M., Pundir, A, 2014, 'Investigation of properties of fluorogypsum - slag composite binders – Hydration, strength and microstructure', Cement & Concrete Composites, no. 45, pp. 227–233

Rodriguez, P. Gonzalez, G. S., Horgnies, M., Calderón, V., 2013, 'Design and properties of plaster mortars manufactured with ladle furnace slag', Materials and Design, no.52, pp. 987–994

Rivera, M. X. R., Alvarado, J. A. C., Valdez, P., Rangel, M. M. J., 2012, 'Modified gypsum compounds: An ecological–economical choice to improve traditional plasters', Construction and Building Materials, no.37, pp. 591–596

Shiyun Zhong, S., Li, J., Ni, K., 2012, 'Properties of mortars made by uncalcined FGD gypsum-fly ash-ground granulated blast furnace slag composite binder', Waste Management, no.32, pp.1468–1472

Shen, W., Zhou, M., Zhao, Q., 2007, 'Study on lime–fly ash–phosphogypsum binder', Construction and Building Materials, no.21, pp. 1480–1485

Yazıcı, H., 2007, 'Utilization of coal combustion byproducts in building blocks', Fuel 86, 929–937

Vimmrova, A., Keppert, M., Michalko, O., Cerny, R., 2014, 'Calcined gypsum–lime–metakaolin binders: Design of optimal Composition', Cement & Concrete Composites, no.52, pp. 91–96