

## CALCIUM SULFATE: AN ALTERNATIVE FOR ENVIRONMENTALLY FRIENDLY CONSTRUCTION

M.A. Guerra-Cossío<sup>1\*</sup>, J.R. González-López<sup>1</sup>, R.X. Magallanes-Rivera<sup>2</sup>, A.A. Zaldivar-Cadena<sup>1</sup>,  
M.Z. Figueroa-Torres<sup>1</sup>

<sup>1</sup> Universidad Autónoma de Nuevo León, Facultad de Ingeniería Civil, Cuerpo Académico de Materiales Alternativos en Ingeniería, Av. Universidad S/N, Ciudad Universitaria, San Nicolás de los Garza, Nuevo León, México, C.P. 66451

<sup>2</sup> Universidad Autónoma de Coahuila, Facultad de Ingeniería, Blvd. Fundadores Km 13, Ciudad Universitaria, Arteaga, Coahuila, México, C.P. 25350

\*Corresponding author; e-mail: [miguel.querracss@gmail.com](mailto:miguel.querracss@gmail.com)

### Abstract

One of the challenges of the construction industry today is to develop and promote the use of environmentally friendly materials. The production and use of Portland cement clinker as a construction material is part of the problem because of its high generation of CO<sub>2</sub> in its manufacture. Therefore, alternative materials that mitigate in some extent this situation become an important task in the development of new materials. The use of calcium sulfate in any form as a construction material has been limited due to its high solubility in water and low development of mechanical strength. However, its use as an alternative cementitious material provides a notable decrease on greenhouse gases produced when it is compared to the manufacture of other hydraulic cementitious materials, since the temperatures required in its manufacturing are relatively low. Therefore, in this study the feasibility of reuse of waste gypsum from the ceramics industry by milling and calcination was evaluated. This calcium sulfate was used as main component in the manufacture of ternary cementitious mixtures. Cementitious test mixtures were manufactured with CaSO<sub>4</sub> synthesized from waste gypsum, ground granulated blast furnace slag and silica fume. Small additions of K<sub>2</sub>SO<sub>4</sub>, Ca(OH)<sub>2</sub> and Portland cement clinker as chemical activators were used. The addition of blast furnace slag and silica fume to the calcium sulfate systems improved its properties and prevented the dissolution in wet environments. The compressive strength achieved by some systems was near 20 MPa at 56 days of curing, showing that this material may be a feasible option for the manufacture of masonry or elements with low structural strength requirements with a proper behavior in wet environments.

### Keywords:

Calcium sulfate; Waste gypsum; Blast furnace slag; Silica fume; Strength; Dimensional stability

## 1 INTRODUCTION

Nowadays, the construction industry, like many other development areas, focuses its objectives towards a sustainable future by reducing the environmental impact on the production and use of construction materials. The ecological/economic need to seek for alternative cementitious materials to Portland Cement, comes from two main reasons [Barcelo 2014]: The high levels of CO<sub>2</sub> produced in the limestone decarbonation process and the high amount of energy needed to reach the 1450°C required by the clinkerization process, mainly promoted by the incineration of fossil fuels. This makes the construction industry one of the most important sources of anthropogenic CO<sub>2</sub> production by manufacturing its principal material. In 2015, more than 4 million tons of Portland Cement were used globally [Geological Survey 2016] and it is estimated

that CO<sub>2</sub> emissions from the cement industry in recent years represented around 5% of total anthropogenic CO<sub>2</sub> [International Energy Agency 2009].

The use of gypsum as a cementitious material provides a lower release of CO<sub>2</sub>, because it does not imply decarbonation of raw material. This decarbonation process represents 60% of the total CO<sub>2</sub> produced in clinker manufacture [Barcelo 2014]. In addition, the energy required for its conditioning in all processes is lower because obtaining a reactive phase by means of calcination requires less temperature than the 1450°C needed for the clinker. Also, because gypsum is a softer material, making it easier to mill. The energy consumption of these processes will not be addressed in this work, but the need to measure these parameters is clear. The main disadvantage of this material is the high

solubility of gypsum in the presence of water, approximately 2 g/L; which restricts its use to indoor environments free of moisture. Likewise, its mechanical strength is very low, compared to that which the portland cement develops. Thus, investigations have been focused on the improvement of parameters such as; mechanical strength, dimensional stability and workability evaluated in composites cured under different conditions using different sources of calcium sulfate and making binary and ternary cements using additions of supplementary cementitious materials such as fly ash, slags, silica fume, metakaolin, etc. [Singh 1995, Singh 1995, Escalante-Garcia 2009, Camarini 2011], these studies have shown that there is feasibility of improving the behavior of the resulting materials. Although, this type of cement composite would not replace Portland cement in many applications, there are many uses where it is possible to use them as an important alternative depending on the development of future research. An example of this is the research by Singh et al. [Singh 1992] who made mixtures of phosphogypsum with Portland cement and a pozzolan, either fly ash or blast furnace slag. The reported compressive strengths were higher in blends with blast furnace slag (35 MPa) than in blends with fly ash (22 MPa) at 28 days of curing. The use that they propose for this material is as raw material for manufacturing of brickwork and as masonry mortar. The improvement of the physical properties of gypsum such as mechanical strength and the decrease of its dissolution are due to the formation of C-S-H type phases that engulfs gypsum crystals, keeping them away from moisture.

## 2 EXPERIMENTAL DETAILS

### 2.1 Materials

Waste gypsum (WG) from spent jiggering molds from a sanitary ceramic industry was used as a source of calcium sulfate. It was conditioned by drying, pulverizing, grinding and calcining for 6 hours at 500°C. Potassium sulfate ( $K_2SO_4$ ) and calcium hydroxide ( $Ca(OH)_2$ ) with industrial grade were used as activators for the calcium sulfate reaction. The granulated blast furnace slag (BFS) was obtained as a by-product from the steel industry, while the silica fume (SF) was a undensified commercial type.

A small amount of clinker (CK) was used in order to act as an alkaline activator for the slag [Ding 2014, Tab. 19], the proposed nomenclature for the systems is related to the percentage content by weight of the main constituents of the mixture (WG-BFS-SF).

### 2.3 Characterization

The compressive strength of 2" cubic samples (ASTM C109) and dimensional stability by length change of prismatic specimens (ASTM C490) were recorded from 1 to 56 days. All specimens were

Tab. 19 Proportioning of mortar mixes (g).

System	50-40-10	50-42.5-7.5	60-32-8	60-34-6	70-24-6	70-25.5-4.5	100-0-0
WG	650	650	780	780	910	910	1300
BFS	520	552.5	416	442	312	331.5	---
SF	130	97.5	104	78	78	58.5	---
Sand	3575	3575	3575	3575	3575	3575	3575

Gruskovnjak 2008, Daimon 1980]. Silica sand with ASTM standards [ASTM International 2011] was used as fine aggregate. always maintaining two SF/BFS ratios, 0.25 and 0.1765, and maximizing the WG content between 50% and 70% by weight.

Tab. 18 shows the chemical composition of raw materials in main oxides obtained by X-ray fluorescence.

### 2.2 Mortar systems preparation

A series of mixtures were proposed varying the contents of the main cementitious materials (WG-BFS-SF) always maintaining two SF/BFS ratios, 0.25 and 0.1765, and maximizing the WG content between 50% and 70% by weight.

Tab. 18 Chemical composition (wt%) and physical properties of raw materials.

Oxide	WG	BFS	SF	CK
Na <sub>2</sub> O	1.298	0.348	---	---
MgO	0.476	9.509	0.197	0.833
Al <sub>2</sub> O <sub>3</sub>	0.840	9.644	---	2.520
SiO <sub>2</sub>	0.861	31.660	96.689	10.395
SO <sub>3</sub>	64.522	3.023	---	1.817
K <sub>2</sub> O	0.025	0.479	0.995	1.062
CaO	31.938	42.919	1.224	77.786
Fe <sub>2</sub> O <sub>3</sub>	0.039	0.542	0.163	4.054
Blaine (cm <sup>2</sup> /g)	5509.4	3514.39	6851.2	1398.5
Density (g/cm <sup>3</sup> )	2.63	2.75	2.18	3.03

Similar SF/BFS relationships have been tested in other investigations [Magallanes-Rivera 2014, Magallanes-Rivera 2014, Magallanes-Rivera 2012], where it was found that the presence of SF hindered the formation of ettringite, however, it can also interfere in the formation of gypsum, affecting the development of mechanical properties at early ages. The activating additives were added in a proportion between 1% and 4% of  $K_2SO_4$  and  $Ca(OH)_2$ , and up to 3% of clinker. The water/cement ratio (w/c) was set at 0.45 for all mixtures due to observed workability, and a ratio of 2.75 parts of sand per 1 part of cementitious material was maintained for all systems as suggested by ASTM standards [ASTM International 2010]. The mixture experimental arrangement is presented in the

maintained in a full immersion curing in water at 23°C until testing or measurement. Some pieces of the crushed cubes were dried by immersion in methanol for 72 hours to stop hydration, then dried for 24 hours at 40°C to remove methanol. Observations were performed under secondary electrons from previously gold-coated fragments on a Jeol JSM-6510LV scanning electron microscope.

### 3 RESULTS AND DISCUSSION

#### 3.1 Compressive strength

The compressive strength results of the cubic specimens are presented in

Fig. 1 as the average of 3 samples per test date (the standard deviations are represented by vertical bars). All systems reported compressive strengths below 5 MPa at one day, however, at 7 days most of the systems exceeded 12 MPa, except for the 100-0-0 and 70-24-6 systems which coincide with the two systems containing the least amount of BFS in its formulation. At 28 days, all systems were already above 17 MPa, with the exception of 100-0-0 and 50-42.5-7.5, which recorded a loss of compressive strength of approximately 8% for both systems. Between 28 and 56 days, the systems seem to tend towards a stabilization, however, two systems stand out because they were close to reaching 20 MPa, which are 50-40-10 (18.97 MPa) and 70-25.5-4.5 (19.21 MPa).

These results exceed by far the typical strength of gypsum plaster of about 4 MPa [Odler 2000], placing this material as a viable alternative for the manufacture of masonry elements or elements with low mechanical requirements, since at 28 days they exceed the minimum compressive strength required by ACI 318-14 (17 MPa) to be considered as structural material. It is possible to observe the solubility of gypsum in wet environments on the behavior of the system 100-0-0 from

Fig. 1 which did not exceed 6 MPa throughout the considered period and that after 7 days its strength decreases to a null value at 56 days, unlike the positive development of the other systems containing BFS and SF. This provides evidence that the composites formed by the reaction of BFS and SF within the cementitious systems, complement the gypsum effectively in the strength gain and dissolution resistance of products in wet environments because these composites shields the gypsum crystals giving them impermeability [Escalante-Garcia 2009, Magallanes-Rivera 2014, Bentur 1994].

#### 3.2 Dimensional stability

The possibility of ettringite formation ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$ ) in this kind of systems is larger, due to the high sulfate content and the presence of reactive Al phases provided by the BFS (the reactive aluminum phases provided by the CK are considered negligible because the quantity is very low). When this ettringite is formed in a hardened matrix, the heterogeneous expansions associated with its formation can cause cracking and peeling, for this reason, it is important to record the evolution of length changes in this class of composites. The results of the monitoring according to ASTM standards [ASTM International 2011], are presented in Fig. 2. In systems with the same gypsum content, those containing more BFS and less SF showed less expansion at the end of 56 days, however, all systems remained below the acceptance limit of 0.020% expansion according to ASTM C-150 standard for mixed cements containing high amounts of  $\text{SO}_3$ , or 0.030% -0.040% for blended

cements exposed to a sulfate solution [ASTM International 2007].

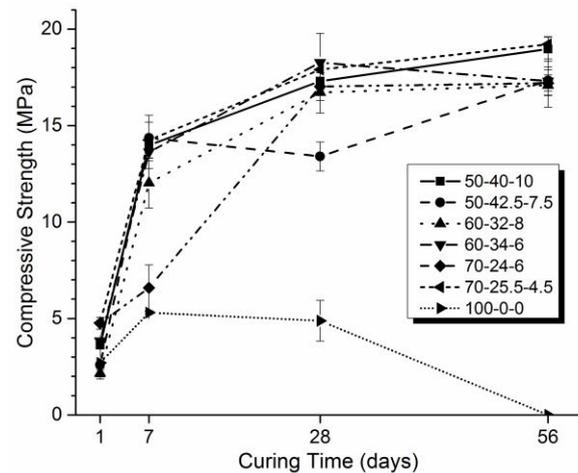


Fig. 1 Compressive strength development of WG-BFS-SF mortars cured under water at 23°C.

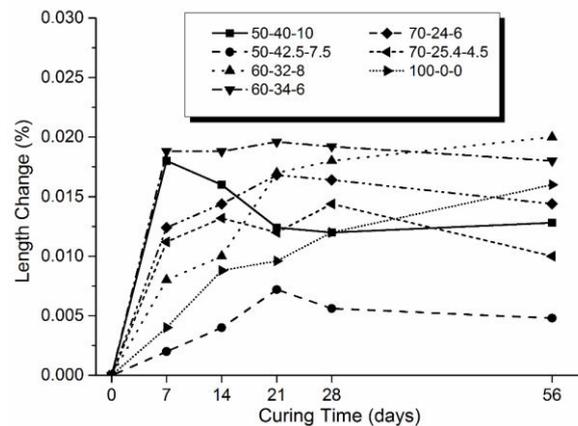


Fig. 2 Expansion of mortar bars cured under water at 23°C.

According to Fig. 2, length changes of the studied mortar bars have stabilized after 56 days. Both systems with 60% WG in their formulation, reported the greatest length change, being 60-32-8 the one with the biggest change of all systems evaluated after 56 days. This coincides with the compressive results, being this the same system that reports the lower compressive strength at the same age. The 100-0-0 system, which was prepared without the addition of BFS or SF, ceased to be measurable at 56 days due to detachment of one of the measuring references, this due to the dissolution of the gypsum. Providing evidence of the decrease in the dissolution degree of the gypsum due to the hydrated phases formed by the BFS and SF.

3.3 Microstructures

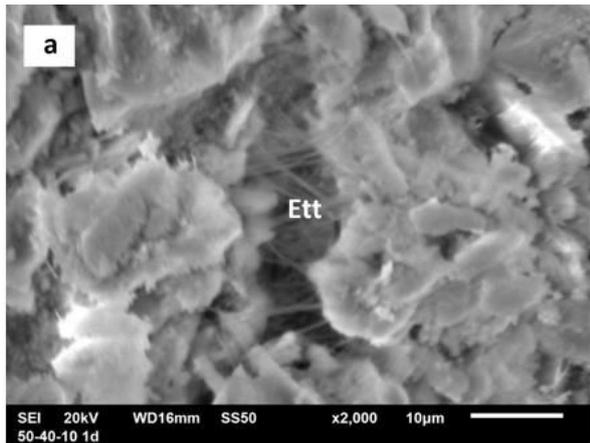


Fig. 3 shows micrographs at 2000-X of fracture surface samples of the 50-40-10 system where it is possible to observe at 1 day (

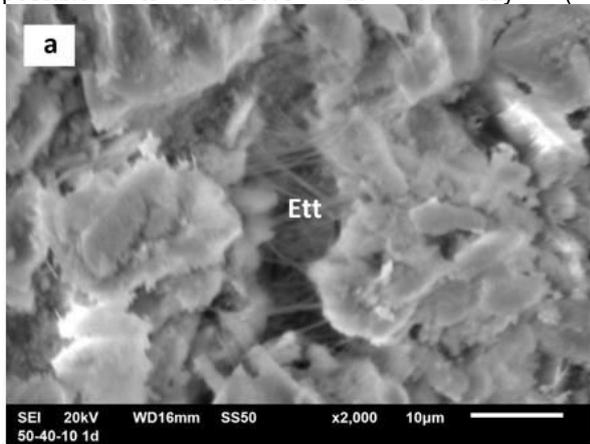


Fig. 3a) well-formed gypsum crystals (DH) between 5 and 10 µm in length, as well as very fine ettringite crystals (Ett) embedded in a still porous matrix. However, at later ages (28 days) it was no longer possible to identify areas of ettringite precipitation, and a less porous microstructure is observed, due to the slow reaction of BFS that filled the pores left by the WG reaction, as evidenced by C-S-H products that engulfed the gypsum crystals in

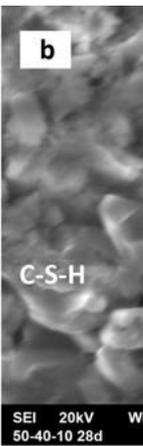
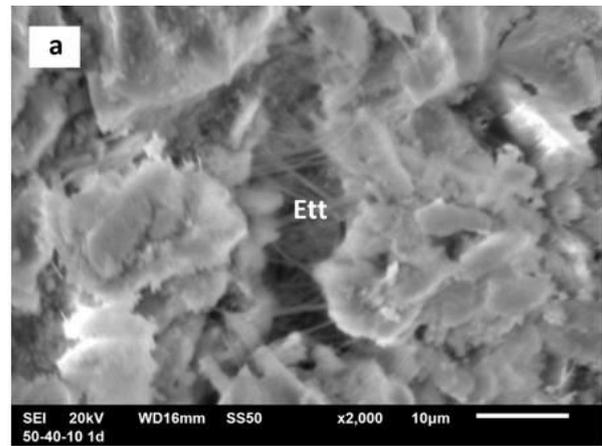


Fig. 3b. Somewhat contrary occurred in the case of the system 70-25.5-4.5, which at 28 days presents a higher formation of ettringite than at early ages, as can be observed in

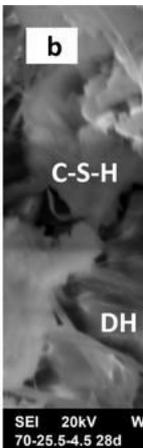
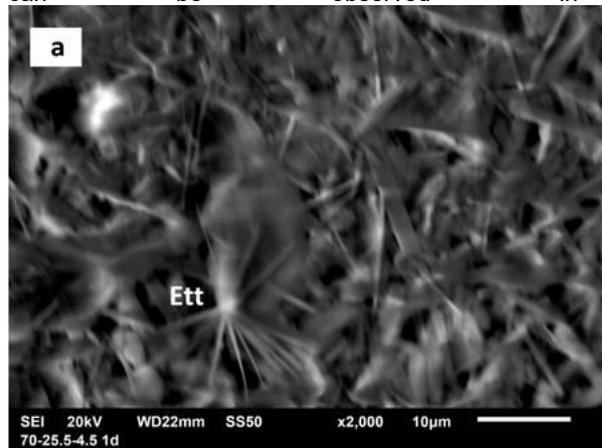


Fig. 4. In this case, there is not enough slag to fill the space initially occupied by water with its reaction products, and because there is space available for its formation, ettringite continued its growth. It is worth mentioning that this system resulted in the highest strength evolution recorded up to 56 days (see Fig. 1). The increase in mechanical properties can then be attributed to the densification of cement matrixes by the formation of gypsum crystals and the formation of ettringite and C-S-H type products [Singh 1992].

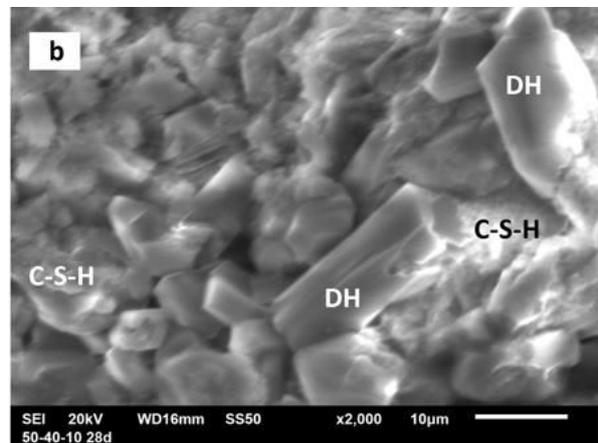
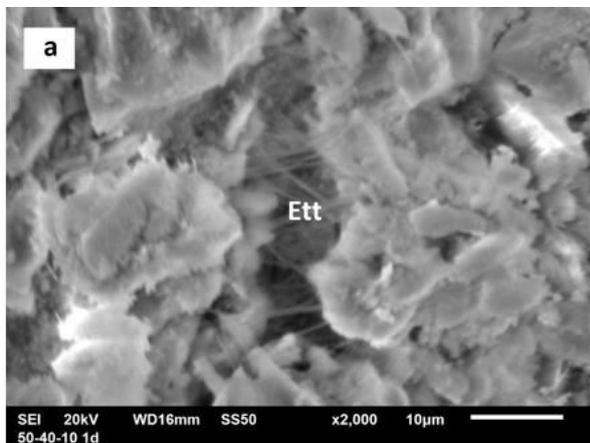


Fig. 3 Scanning electron microscopy images obtained from fractured samples of 50-40-10 system at a)1 day and b)28 days. Secondary electron mode images.

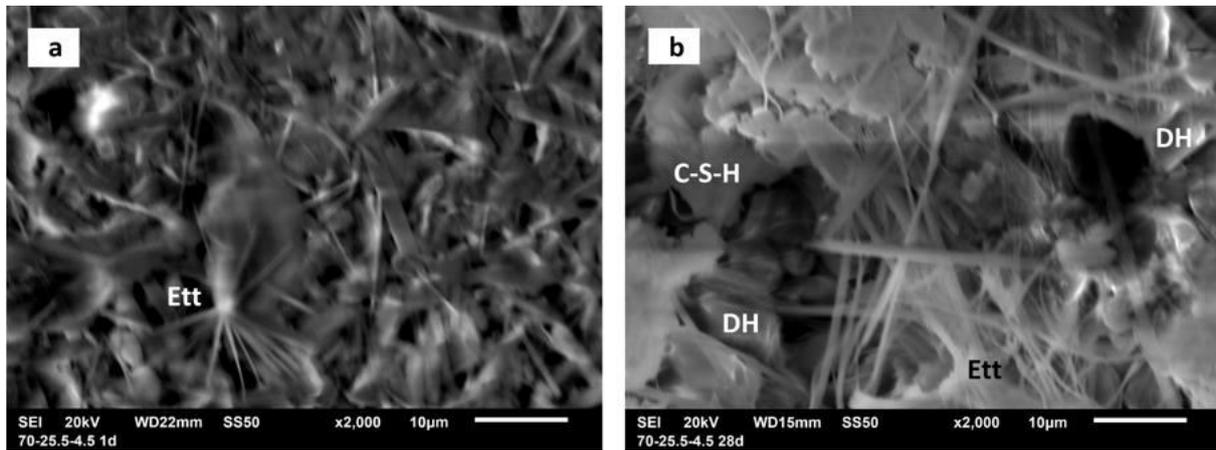


Fig. 4 Scanning electron microscopy images obtained from fractured samples of 70-25.5-4.5 system at a) 1 day and b) 28 days. Secondary electron mode images.

#### 4 SUMMARY

The addition of BFS and SF to WG systems was beneficial for both, the development of mechanical properties and to avoid the dissolution of gypsum in wet environments and the consequent loss of properties at later ages. The presence of ettringite was corroborated by SEM observation; however, only the 60-34-6 system showed a 5.2% decrease in compressive strength between 28 and 56 days of curing. The compressive strength obtained by the composites after 56 days were ~20 MPa; which is a feasible alternative for the manufacture of masonry elements or elements with low mechanical requirements, with a suitable behavior in wet environments. Future works should aim on the analysis of failure mechanisms of elements made from these cementitious materials such as masonry pieces or walls. Determining the mechanism of SF to reduce the formation of ettringite in these systems would open the possibility of replacing it with some other material, because this is considered expensive.

#### 5 ACKNOWLEDGMENTS

To the Secretary of Public Education (SEP) for the support to UANL-CA-370 for the scholarship granted to carry out this research, and for the financing granted for project dsa/103.5/16/9762.

#### 6 REFERENCES

- [ASTM International 2007] Standard Specification for Portland Cement. Annual Book of ASTM Standards, 2007, 04.01, ASTM C150/C150M-09.
- [ASTM International 2010] Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens). Annual Book of ASTM Standards, 2010, 04.01, ASTM C109/C109M-08.
- [ASTM International 2011] Standard Practice for Use of Apparatus for the Determination of Length Change of Hardened Cement Paste, Mortar, and Concrete. Annual Book of ASTM Standards, 2011, 04.01, ASTM C490/C490M-09.
- [ASTM International 2011] Standard Specification for Standard Sand. Annual Book of ASTM Standards, 2011, 04.01, ASTM C778-06.

[Barcelo 2014] Barcelo, L.; Kline, J.; Walenta, G.; Gartner, E.; Cement and carbon emissions. *Materials and Structures*, 2014, 47, 6, 1055–1065.

[Bentur 1994] Bentur, A.; Kovler, K.; Goldman, A.; Gypsum of improved performance using blends with Portland cement and silica fume. *Advances in Cement Research*, 1994, 6, 23, 109–116.

[Camarini 2011] Camarini, G.; De Mito, J.A.; Gypsum hemihydrate – cement blends to improve renderings durability. *Construction and Building Materials*, 2011, 25, 11, 4121–4125.

[Daimon 1980] Daimon, M.; Mechanism and Kinetics of Slag Cement Hydration. In *7th International Congress on the Chemistry of Cement*, Paris, 1980, 2-8.

[Ding 2014] Ding, S.; Shui, Z.; Chen, W.; Lu, J., et al.; Properties of Supersulphated Phosphogypsum-slag Cement (SSC) Concrete. *Journal of Wuhan University of Technology-Mater. Sci. Ed.*, 2014, 29, 1, 109–113.

[Escalante-Garcia 2009] Escalante-Garcia, J.I.; Magallanes-Rivera, R.X.; Gorokhovskiy, A.; Waste gypsum – blast furnace slag cement in mortars with granulated slag and silica sand as aggregates. *Construction and Building Materials*, 2009, 23, 8, 2851–2855.

[U.S. Geological Survey 2016] U.S. Geological Survey; Mineral commodity summaries, 2016, 44.

[Gruskovnjak 2008] Gruskovnjak, A.; Lothenbach, B.; Winnefeld, F.; Figi, R., et al.; Hydration mechanisms of super sulphated slag cement. *Cement and Concrete Research*, 2008, 38, 7, 983–992.

[International Energy Agency 2009] Cement Technology Roadmap 2009 Carbon emissions reductions up to 2050, 2009.

[Magallanes-Rivera 2014] Magallanes-Rivera, R.X.; Escalante-Garcia, J.I.; Anhydrite / hemihydrate-blast furnace slag cementitious composites: Strength development and reactivity. *Construction and Building Materials*, 2014, 65, 20–28.

[Magallanes-Rivera 2014] Magallanes-Rivera, R.X.; Escalante-Garcia, J.I.; Hemihydrate or waste anhydrite in composite binders with blast-furnace slag: Hydration products, microstructures and dimensional stability. *Construction and Building Materials*, 2014, 71, 317–326.

[Magallanes-Rivera 2012] Magallanes-Rivera, R.X.; Juarez-Alvarado, C.A.; Valdez, P.; and Mendoza-

Rangel, J.M.; Modified gypsum compounds: An ecological – economical choice to improve traditional plasters. *Construction and Building Materials*, 2012, 37, 591–596.

[Odler 2000] Odler, I.; *Special Inorganic Cements. Modern Concrete Technology Series 8* (E & FN Spon), 2000.

[Singh 1992] Singh, M.; Garg, M.; Investigation of a durable gypsum binder for building materials.

*Construction and Building Materials*, 1992, 6, 1, 52–56.

[Singh 1995] Singh, M.; Garg, M.; Activation of gypsum anhydrite-slag mixtures. *Cement and Concrete Research*, 1995, 25, 2, 332–338.

[Singh 1995] Singh, M.; Garg, M.; Phosphogypsum - Fly ash cementitious binder - Its hydration and strength development. *Cement and Concrete Research*, 1995, 25, 4, 752–758.