



Microstructure and mechanical properties of composite cements: reactivity of pozzolanic and hydraulic cementitious materials

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ABSTRACT

This research was focused on the use of pozzolanic and hydraulic additions as partial replacement of Portland cement. In order to evaluate the mechanical properties, microstructure and hydration reactions of the composite cements phases, granulated blast furnace slag, fly ash, metakaolin, and geothermal silica were used as replacement materials. The following conditions were utilized: replacement levels of 50, 40 and 30% of the mentioned materials, a water/cementitious materials ratio of 0.4, curing temperatures of 20 and 50°C and curing intervals from 3 to 180 days. The results indicated a high degree of reactivity of replacement materials and an increase in the mechanical properties up to 200% compared to pure cement, resulting in a matrix of more dense reaction products and thus a reduction in porosity.

Keywords: microstructure; reactivity; mechanical properties; industrial byproducts.

RESUMEN

Este trabajo de investigación se centró en el uso de adiciones puzolánicas e hidráulicas como sustituto parcial del cemento Portland. Con la finalidad de evaluar las propiedades mecánicas, microestructurales y reacciones de hidratación de los cementos compuestos, se emplearon como sustitutos de cemento Portland: escoria granulada de alto horno, ceniza volante, metacaolín y sílice geotérmica. Se utilizaron niveles de reemplazo de 50, 40 y 30% de los materiales anteriormente mencionados, una relación agua/material cementante de 0.4, temperaturas de curado de 20 y 50°C, por un periodo de hasta 180 días. Los resultados indicaron un alto grado de reactividad de los materiales de reemplazo y un incremento en las propiedades mecánicas hasta en un 200% en comparación con el cemento puro, lo que impactó en una matriz de productos de reacción más densa y por tanto en una reducción en la porosidad.

Palabras clave: microestructura; reactividad; propiedades mecánicas; subproductos industriales.

RESUMO

Esta pesquisa tem como objetivo a análise do uso de adições pozolánicas e hidráulicas como substituto parcial do cimento Portland. Com a finalidade de avaliar as propriedades mecánicas, microestrutura e as reações de hidratação dos cimentos compostos, utilizou-se como elemento substituinte do cimento: escória de alto forno, cinza volante, metacaulim e sílica ativa.

Foi utilizadas proporções de 50, 40 e 30% dos materiais anteriormente citados, com uma relação água/material cimentício de 0,40, temperaturas de cura de 20°C a 50°C, por um período de até 180 dias. Os resultados indicaram um alto grau de reatividade dos materiais de substituição e um incremento das propriedades mecánicas de até 200% em comparação com o cimento puro, resultando em uma matriz mais densa e, portanto uma redução na porosidade.

Palavras-chave: microestrutura; reatividade; propriedade mecânica; subprodutos industriais.

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1. INTRODUCTION

Portland cement industry has experienced considerable expansion in recent years due to the growth of civilization and industrial and technological development. The consumption of Ordinary Portland Cement (OPC) has dramatically increased in recent years: from approximately 1.5 billion tons (Global Cement Information System) in 1998 of 3.4 billion tons in 2013 (Global Cement Report). If the world's cement production continues with this trend the CO₂ emissions could reach 3,000 million tons (Global Cement Report) during the first quarter of the XXI century. The cement industry has established sustainability as a primary focus together with the achievement of economic prosperity, social responsibility and environmental care. Nowadays, it is a worldwide concern to try to find new ways to reduce the amounts of greenhouse gases generated by the production of OPC. In order to reach this goal, one of the most important research is focused in the partial replacement of cement or clinker substitution with supplementary cementitious materials, as pozzolans or latent hydraulic materials, that reduce significantly the damage caused to the environment, specifically the 7% CO₂ emissions caused by the cement production. The use of alternative materials in the cement industry; as with aluminosilicate raw materials, waste from metallurgical plants, agricultural and waste power plants, has proven to increase sustainability an effective way.

Moreover, according to the literature, several pozzolanic materials rich in silica, such as silica fume (SF), fly ash (FA) class F or rice husk ashes; which in addition to provide pozzolanic behavior, accelerate the initial hydration of Portland cement and improve its mechanical properties (Gomez-Zamorano and Escalante-Garcia, 2009). Based on that, the aim of this study was to investigate the effect of geothermal silica (GSW) since it has similar properties to those pozzolanic materials.

Thomas et al. (1999) studied the durability of ternary mixtures with Portland cement, SF and a wide range of FA content. They reported that the FA with high CaO content is generally less effective in inhibiting the alkali-silica reaction and sulfate attack compared to the FA class F. Furthermore, in this study it was shown that higher levels of replacement (around 60%) are required to control the expansion due to alkali-silica reaction, and relatively small additions of SF (3 to 6%) were effective in reducing the expansion. It was shown in this study that there is a synergistic effect between FA and SF; FA improved the workability, while SF compensated the relatively low early strength provided by FA. The results indicated that the blended cements had a very high resistance to chloride ions penetration, which is an important feature when the concrete is exposed to those conditions during service.

Bijen (1996) highlighted the use of blast furnace slag and the FA as replacement materials, showing an improvement in the corrosion, alkali silica reaction, and sulfate attack resistances, together with a reduction in the rate of penetration of chloride ions.

Additionally, Gesoglu et al. (2009) reported that an increase in the amount of FA content decreased the compressive strength self-compactable concrete containing FA, limestone and blast furnace slag, however in the presence of SF the mechanical strength was improved.

Gutteridge and Dalziel (1990), as well as Taylor and Mohan (1985) studied the hydration process OPC pastes replaced with slag and FA; they pointed that the fine particle size of the FA and slag enhanced the cement hydration, favoring the heterogeneous nucleation of the hydration products. This decreased the activation energy and accelerated the reaction of the whole system.

Talero and Rahhal (2009) conducted a study on the effect of SF and two types of metakaolin (MK) in the heat of hydration of cement compounds with different contents of C₃A and C₃S. According to their results, the pozzolanic activity of the two MK was dependent on its amorphous structure and the content of Al₂O₃ in MK chemical composition. The high amorphous fraction content in the SF increased the initial hydration reactions of the OPC. For the case of the MK the improvement of the

hydration reactions of the cement was related with the Al_2O_3 content. Additionally, the amount of heat produced per gram of cement was higher for those containing a larger amount of C_3A .

Snelson et al. (2008) investigated the evolution of the hydration heat in OPC samples partially replaced with MK and FA. Their results showed a decreased hydration heat with the increase in the FA content. Similar results were observed in the presence of MK. For both systems the main factor controlling the hydration kinetics of the OPC was the water requirement of the pozzolan. For the pastes containing both, FA and MK, the pozzolanic activity of MK increased the hydration heat reported.

It is worth nothing that the information regarding with the use of geothermal silica waste as a replacement material for Portland cement, is very limited. Nevertheless, it is estimated (US Patent 1990) that around 80% of the geothermal plants in the world have problems with the generation and accumulation of this waste. In addition, according to previous reports (Gomez-Zamorano et al, 2004; Iniguez, 2008), this material has an enormous potential to be used as replacement material of Portland cement, and is not currently used systematically.

Thus, based on the previously described results, this paper shows the hydration process of OPC in presence of a wide range content of pozzolanic and hydraulic materials, cured at moderate and high temperatures (Gomez-Zamorano, 2004, Battagin et al, 1997), as 20 and 50°C up to 180 days. Replacements levels of 50, 40 and 30% (mass) of blast furnace slag, fly ash, metakaolin and geothermal silica and a water/binder ratio of 0.4 were used.

2. MATERIALS AND EXPERIMENTAL METHODOLOGY

The materials selected for this project were Portland cement that was obtained from Cemex México and four replacement materials: (a) two different types of ground granulated blast furnace slag (SLAG1 and SLAG2) with different chemical composition, hence different hydraulic index (see table 1a) and amorphous phase percentages as shown in the figure 1, (b) geothermal silica waste obtained from the Comision Federal de Electricidad in Baja California, Mexico, (c) fly ash type F, and (d) metakaolin. The main characteristics of the GSW were: chemical composition rich in amorphous silica with traces of sodium and potassium chlorides, the particle size in the range of 10-50 nm (see Figure 2), white color, and density of $2.1\text{g}/\text{cm}^3$. The chemical composition analyzed by X-Ray Fluorescence (XRF) is shown in Table 1. The blast furnace slags were characterized by means of quantitative X-Ray Diffraction (XRD) in order to estimate the percent amorphous fraction; obtaining 97% for SLAG1 and 82% for SLAG2. Different systems of blended and neat cement pastes with w/c ratio of 0.4 and 0.4% of superplasticizer were prepared and cured up to 180 days. All the experiments were hydrated at 20 and 50°C. The replacement levels used were up to 50% of OPC as can be seen in Table 1. The GSW was added to the systems as an alkaline suspension, to modify the pH in the mixes, the rheology of the pastes and the content of Ca and Si ions in the pore solution, which could directly affect the final solid and aqueous phase composition of the blended cements. After the hydration periods of 3 to 180 days, the samples were characterized by means of compressive strength: then solid fractions of the samples were crushed washed in acetone and dried at 50°C in order to stop the hydration reactions. TGA/DTA analyses were carried out in open vessel with helium flux using 10 mg of powdered cement at 20°C/min up to 980°C. The XRD experiments were performed to evaluate the mineralogical composition of the powdered samples, scanned between 5 and 85°2 θ . The microstructure was analyzed using backscattered electron images in scanning electron microscopy (SEM).

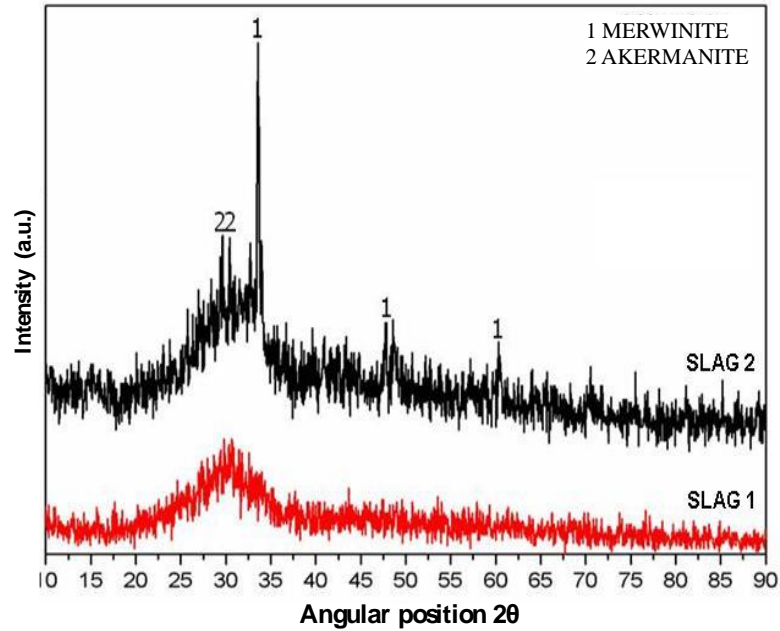


Figure 1. XRD patterns of the both types of slags (SLAG 1 and 2)

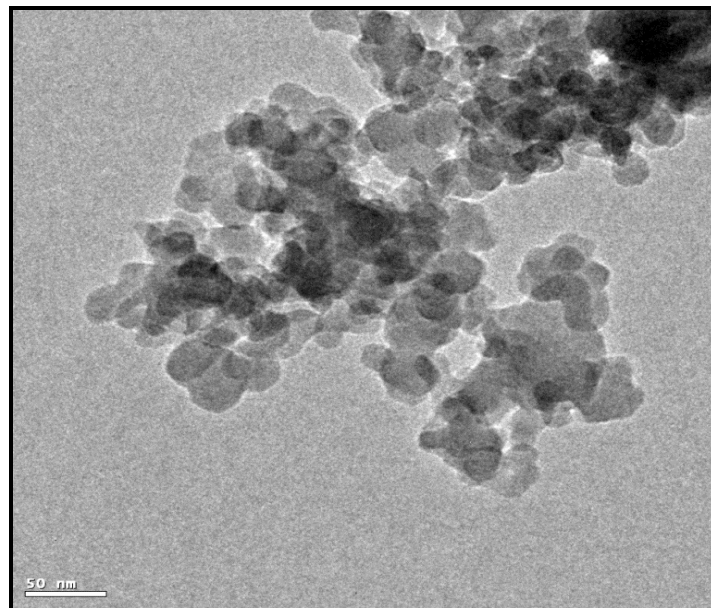


Figura 2. Micrograph of the geothermal silica waste by transmission electron microscopy at 50000X

3. RESULTS AND DISCUSSION

3.1. Compressive strength.

The results of compressive strength for all cements with the two different slags cured at 20 and 50°C respectively are presented in Fig 3. All the blended cements showed a reduction in the compressive strength development at early ages compared with the OPC. However, at long hydration periods the evolution of the values in the blended cements shows significant differences. The highest strengths were those with 50% of replacement, 10% of GSW and the SLAG1 cured at 20°C. This behavior is

an agreement with Verbeck and Helmuth (1968) who claimed that at lower temperatures the hydration products have enough time to diffuse and precipitate uniformly in the cement paste forming a relatively compact matrix of hydration products. Nevertheless, at higher hydration temperatures, the reaction rate is higher than the diffusion rate and most of the hydration products remain near to the anhydrous cement grains, leaving the interstitial space relatively open. Following from this, after 28 days of hydration, the strength of the neat cement cured at 50°C decreases, this phenomenon has been previously reported for neat and blended cements with GSW (Beatriz de León Malacara, 2007 and L. Y. Gómez-Zamorano et al., 2004). In a general way, the pozzolanic silica additions accelerated the hydration of the OPC as nucleation sites at the beginning and then by the production of CSH consuming the CH, this behavior was pointed out by (Gomez-Zamorano et. al., 2004, Iñiguez-Sanchez et. al. 2012). Nevertheless previous reports indicate that an increase in the replacement level higher than 30% with pozzolanic additions with small particle size could be prejudicial to the hydration process (Mehta, P.K., 1989).

Table1. (a) Chemical composition and surface area (BET) of the materials used and (b) experimental systems.

(a)

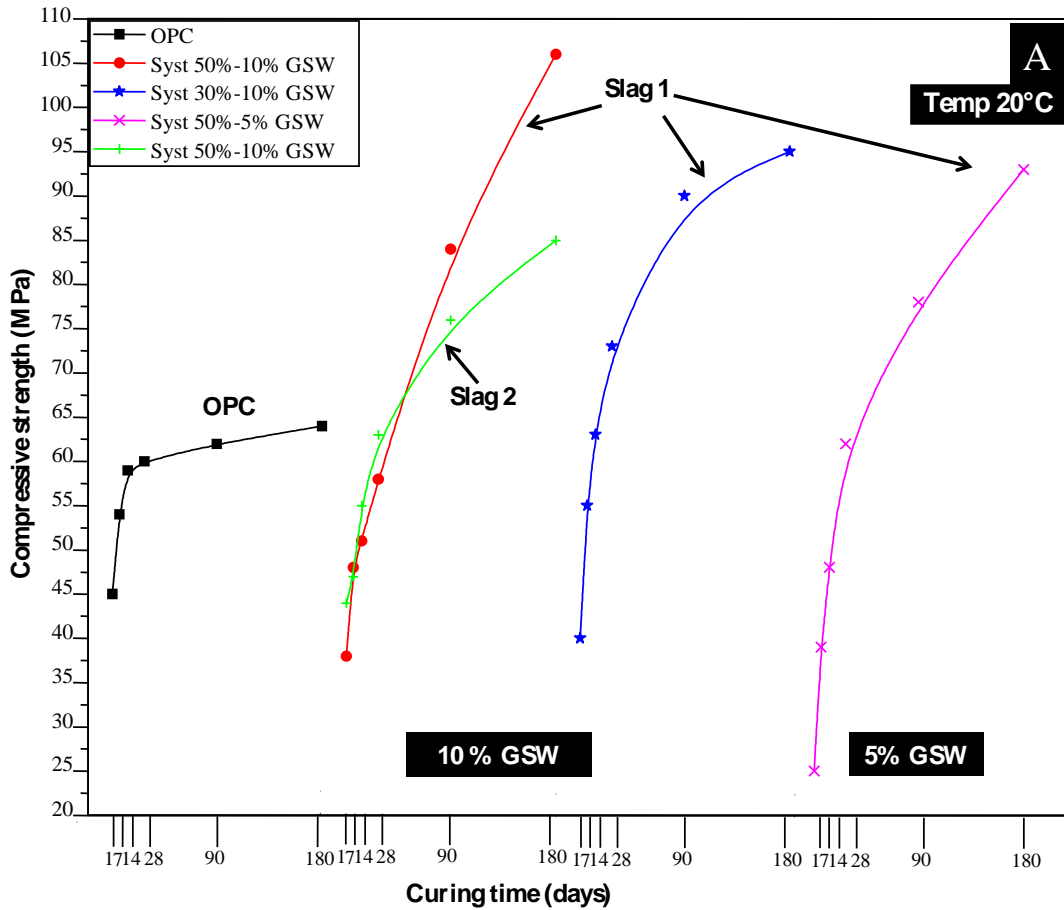
Oxide (%p)	OPC	SLAG1	SLAG2	FA	GSW	MK
iO ₂	18.69	35.55	31.49	60.67	94.76	58.71
Al ₂ O ₃	4.73	9.97	9.41	26.08	0.17	23.54
Fe ₂ O ₃	2.17	1.06	0.51	5.47	0.03	1.86
CaO	64.55	38.84	43.45	2.68	0.41	7.18
MgO	1.77	7.86	8.78	0.74	-	0.14
TiO ₂	0.21	2.38	1.42	1.23	-	0.36
Na ₂ O	0.25	0.42	0.32	0.72	0.29	0.58
K ₂ O	0.69	0.57	0.44	1.8	0.22	0.81
MnO	0.07	0.89	1.26	-	0.04	-
P ₂ O ₅	0.12	-	-	-	-	0.5
Cl	-	-	-	-	0.05	-
SO ₃	4.12	2.41	2.89	0.53	-	1.68
PPI	3.60	-	-	-	4.96	2.89
BET* (m ² /kg)	523	494	-	446	665	-

(b)

System	Replacement level (%)						TEMP
	OPC	SLAG1	SLAG2	FA	GSW	MK	
T1	100	-	-	-	-	-	20°C
S1	50	30	-	5	10	5	
S3	70	10	-	5	10	5	
S4	50	30	-	10	5	5	
S7	50	-	30	5	10	5	
T7	100	-	-	-	-	-	50°C
S13	50	30	-	5	10	5	

* Surface area

In the system with the lowest amount of GSW and the higher amount of FA (see S4) the early gain of compressive strength presented a reduction compared with the rest of the systems. This behavior could be related with the poor reaction of the FA, which at the initial stages could only be helping in the rheology of the pastes, but not contributing with sites of nucleation and acceleration of the cement reactions, which could lead a diminution of the early compressive strength values; however, the final values of the three systems with SLAG1 presented a considerable increase in the mechanical properties compared with the neat cement (see S1 and S3). The effect of SLAG2 is also showed in the graph, with a diminution in the mechanical strength compared with SLAG1, but as the rest of the systems with higher properties compared to the neat cement. This behavior was possible related with the lower percentage of amorphous fraction of the SLAG2, reducing its reactivity in the system, as previously reported by Escalante et al. 2001. Fig.3b presents a comparison between the OPC and blended cements cured at 50°C; at early ages the mechanical properties are higher for the OPC, although after 28 days this behavior was reverted, observing an increase in the compressive strength for the blended cements cured at room temperature, this effect could be due to the phenomenon explained above.



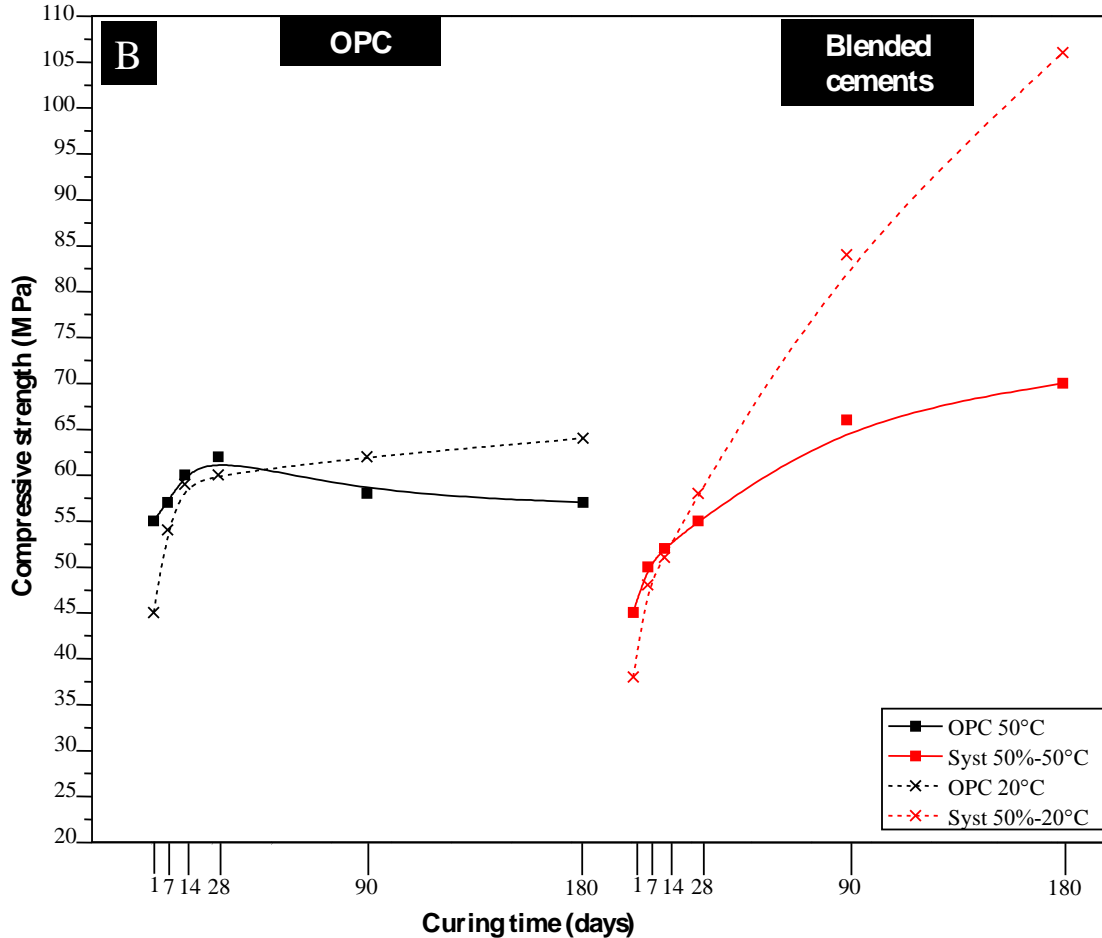


Figure 3. Compressive strength of: (a) samples cured at room temperature and (b) comparative with the increase in the temperature.

3.2 X-Ray diffraction.

The cement hydration was followed by means of the estimation of the changes in the peak intensity of crystalline phases in the XRD patterns and changes observed in TGA/DTG analyses.

Figure 4 shows the X ray diffraction patterns of the neat and blended cements with 50 and 30% of replacement, cured at 20°C up to 28 days. From Figure 4 is possible to observe that the hydration products formed are similar in the different samples. Nevertheless, the main difference observed between neat and blended cements is the consumption of the calcium hydroxide (CH) due to the pozzolanic reaction that could be related with the increase in the compressive strength values. Following from this, the strong pozzolanic behavior was affected by the silica load (red line, system S1 with 10% of GSW and pink line, system S4 with 5% of GSW) and curing temperature, with the highest CH consumption for the S13 system (10%GSW and 50°C). This evidenced the pozzolanic behavior of the GSW, which is similar to those reported by other authors with different pozzolanic materials (V. Yogendran et al, 1991).

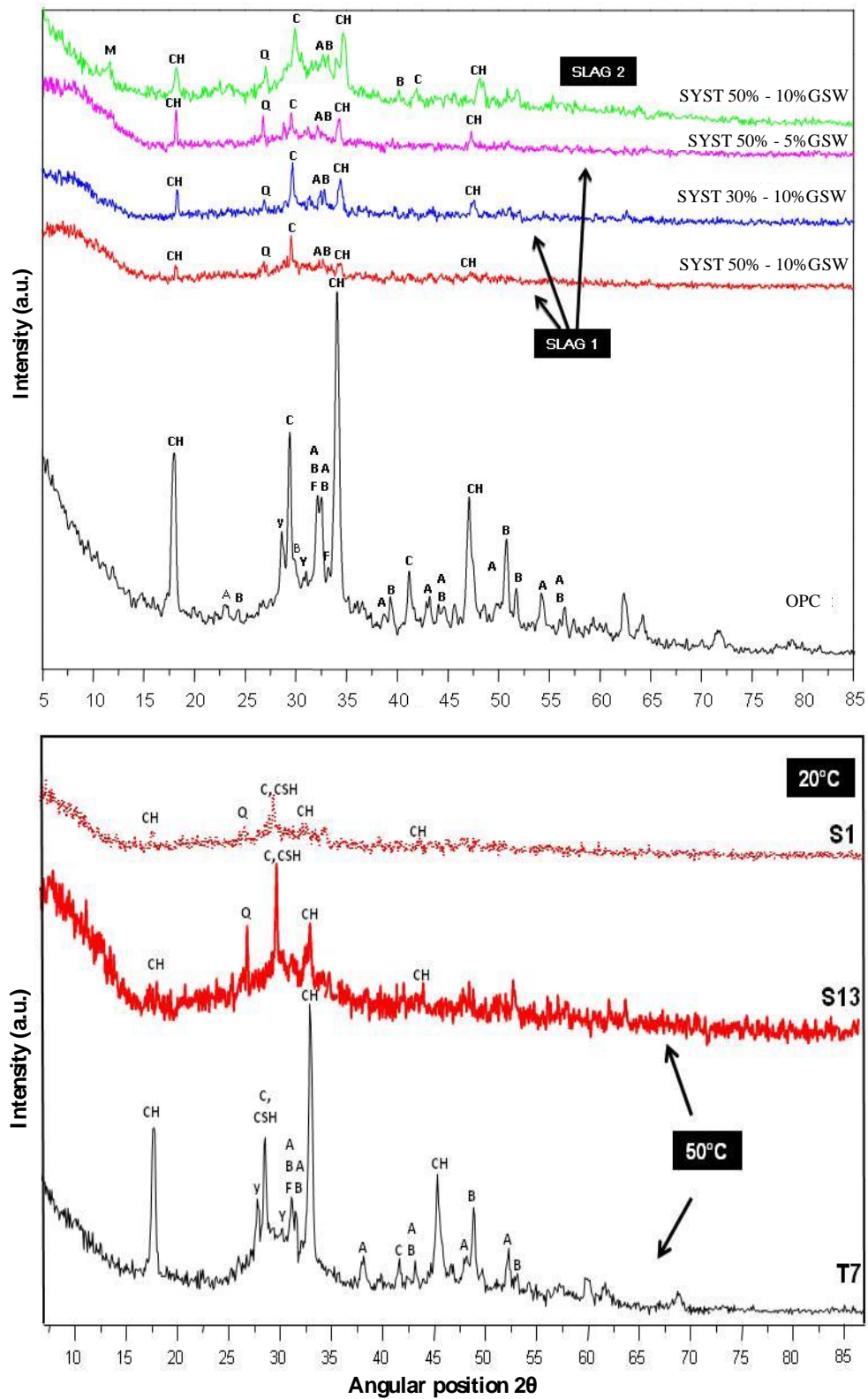


Figure 4. X ray diffraction results for all the systems at (a) room temperature and (b) comparative at 20 and 50°C. M=monosulphoaluminate, A=alite, B=belite, Q=Quartz, C=calcite, CH=Calcium hydroxide, Y=gypsum, F=ferrite

3.3 Thermal analysis.

As mentioned before, the TGA analyses were performed to follow the hydration of the neat and blended cements. The amount of ettringite, gypsum and portlandite was estimated from the weight loss between 50-110, 110-140 and 440-500°C respectively. Also, the differential thermal analysis (DTA) showed the formation of C-S-H gel, AFm, Hydrocalcite and Portlandite phases as observed in the Fig. 5. Additionally, the data indicated a decrease of calcite but a formation of calcium monocarbonate (C_4AcH_{11}) in all of the blended cements compared with the OPC. Kuzel et al. (1996) reported the formation of monocarboaluminates in the presence of carbonates, which prevents the formation of ettringite, and generation of monosulphoaluminate, as indicated by the S7 system (green line). This behavior was also observed in the XRD results from fig 4.

The pozzolanic and hydraulic reaction of the replacement materials in all the blended cements is reflected by the increase in the amounts of C-S-H gel in the range of 105-200°C and the decrease of CH in the range 450-550°C, indicating the strong pozzolanic behavior of the supplementary cementitious materials. The presence of calcite was also observed at approximately 750°C, at the same time the presence of a second peak at 700°C which refers of CO_2 liberation, indicating the formation of calcium monocarboaluminate, as mentioned before. The reduction in the AFt content was also observed for the blended cements.

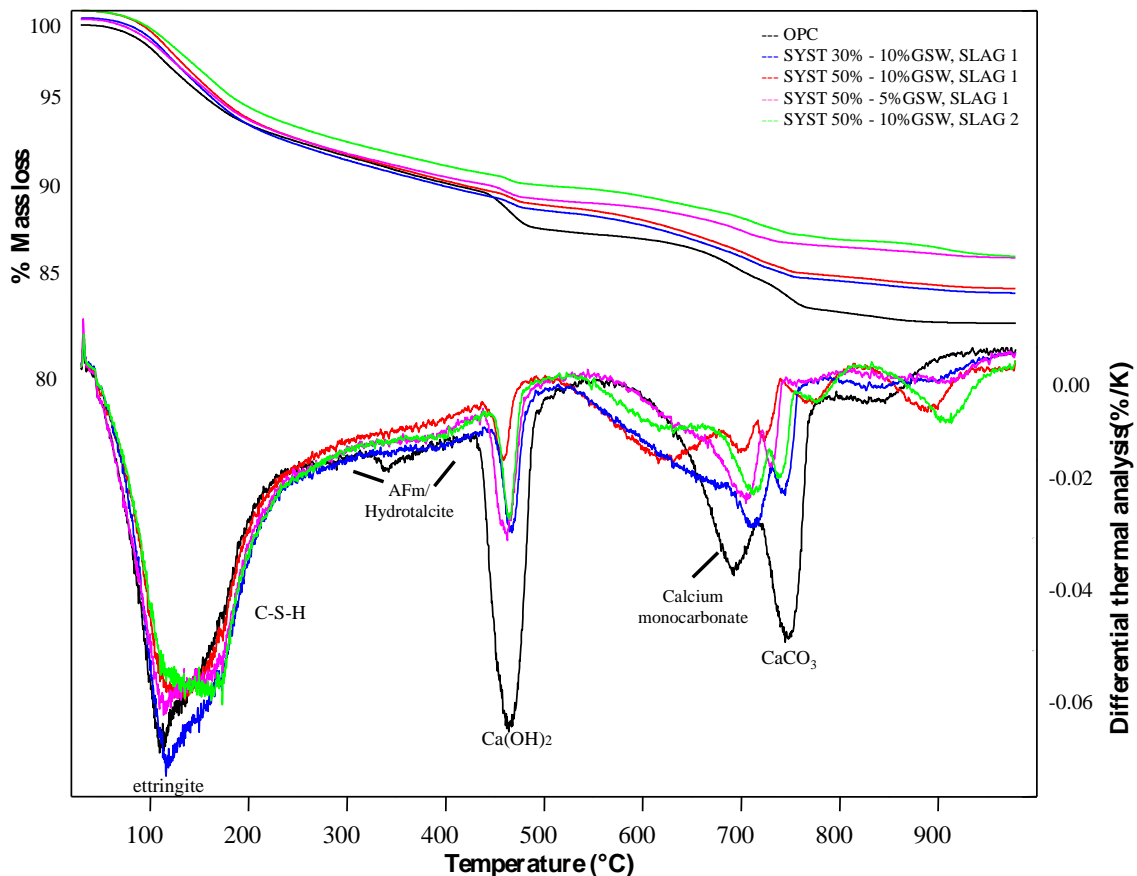


Figure 5. Thermal analysis results of the systems with both slags cured at 20°C.

3.4 Scanning Electron Microscopy.

The samples of neat and blended cements were hydrated for 90 days at 20°C and analyzed by means of backscattered electron images (see Fig. 6). The main features observed are those commonly

presented in cement pastes with water/solids ratio of 0.40, with a fraction of the cement unreacted, with calcium hydroxide crystals (for the neat cement) and porosity dispersed throughout the microstructure. All the blended cements (Fig. 6.S1, 6.S7 and 6.S13) showed a similar microstructure and chemical evolution, with cement grains already reacted and a more compact matrix compared to the neat cement (Fig. 6.T1), which is related with the increase in the compressive strength as pointed out above. The reduction in the porosity could be due to: A) the filler effect of FA and GSW, but also the latter as nucleation sites due to its nanometric particle size, B) calcium hydroxide consumption by the pozzolanic reaction forming new hydration products. Fig. 6.S13 shows the microstructure of a blended cement (system 13) cured at 50°C, where it is possible to observe some cement grains with irregular rims due to the onset reaction, which occur so fast at elevated temperature that the cement had not enough time to generate the hydration products and the porosity was increased, nevertheless this behavior is not comparable with the neat Portland cement. A similar pattern was observed in samples with SLAG2 (figure 6.S7) as with the presence of SLAG1 with similar hydration products and a reduction in the porosity.

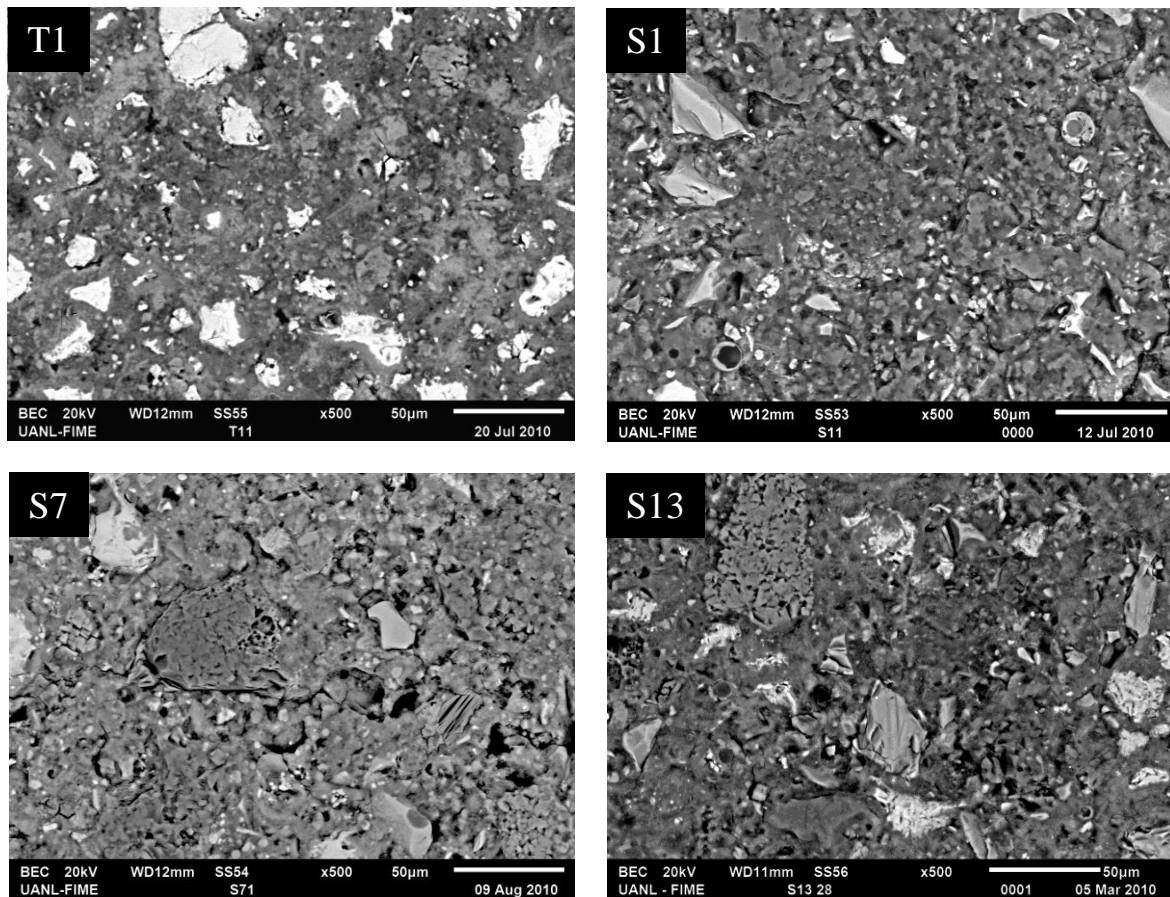


Figure 6. Backscattered electron images from scanning electron microscopy, illustrating the microstructure of samples cure at room temperature for neat cement (T1), blended cement with 50% of replacement and SLAG 1 (S1), blended cement with 50% of replacement and SLAG 2 (S7) and blended cement with 50% of replacement and SLAG 1 at 50°C (S13).

4. CONCLUSIONS

- According to the results, the reactivity in the blended cements is strongly affected by the amorphous fraction of the SLAG 1, providing an enhancement of the compressive strength in the systems with high replacement levels.
- At the same time, the use of high concentrations of a suspension of GSW has been prove a favorable evolution and reactivity of hydration products, generating higher nucleation sites and obtaining more compact matix and better properties in the microstructure.
- The strong pozzolanic behavior of the GSW was evidenced by the consumption of the CH and generation of a higher quantity of C-S-H gel, as showed in the XRD and TGA results. The high reactivity of this material is due to its composition, high fineness and its amorphous state, the use of this material as a suspension promoted excellent physical, chemical and mechanical properties.
- In general, the use of high levels of hydraulic and pozzolanic materials in the formation of quaternary cements, produced an increase in the mechanical properties of the systems, as well as in the hydration reactions, providing a more compact microstructure by means of the reduction of the porosity.

5. ACKNOWLEDGEMENTS

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