Durability of H-class cement and blast furnace slag-based cementitious composites

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The usage of residual slag generated in the steel making process has been highlighted both as an ecological and/or economical alternative for the production of innovative cement and/or special cement composites. However, the effect of granulated blast furnace slag (GBFS) on the durability of cement still requires experimental research. This paper discusses the durability of H-class cement considered suitable for cementing oil wells, which was mixed with blast furnace slag and activated with NaOH alkali. This research has been conducting in accordance to the methods established under Mexican standards for assessing the technical suitability in developing an alternative cementitious product. The characterization of the products thus obtained was carried out through chemical analyses, compressive resistance and sulfate attack testing. The microstructure of obtained composites was also analyzed by scanning electron microscopy. Results show a limited durability of the cementitious composites, revealing a decrease in their mechanical resistance to compression as the percentage of slag increases, as well as a poor performance when exposed to sulfates media. As the slag percentage in H-class cement was increased a certain reduction on the expansion level of the composite was observed.
Keywords: cementitious composites, aggregated alkali, granulated blast furnace slag, durability, resistance to sulfates

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Introduction

The durability of cement or derivatives thereof may be defined as the capacity of a cement product to resist the action of external forces or destabilizing systems to chemical and/or physical-mechanical attack. Depending on the quality and application method of cement and products derived there from, they might be vulnerable when exposed to aggressive environments which foster important chemical reactions, such as those typical in the cement decarbonization. The formation of cracks and accelerated erosion of these materials are other examples associated with durability. Traditionally, durability of cement has been correlated to its strengthening characteristics, specifically with its compression resistance. However, in several publications [1–10], it has been shown that this parameter is not enough to fully characterize the durability of cement. Analyzing durability of concrete and/or its products can be a complex task, depending on every exposure environment and/or service condition. The type of material used and the mixture design, the additives features, the production technique and the construction process can all be determining factors to consider in the analysis. In practice, there are environmentally friendly alternatives for cement to extend its lifetime, which include the addition of inorganic materials (i.e. blast furnace slag, natural puzzolans, volcanic ash, silica fume, calcined clay, among others) that have similar composition to cement. These mixtures are referred to as cementitious composites, in which its major components are cement and one or more inorganic materials that take part in the hydration reactions and therefore make a substantial contribution to the hydration products [1]. According to Osborne [2] the factors that may affect durability are setting time and the type of cement being used; as well as the Alite (C_3A) phase content and the percentage of alumina present in the slag. Tailing et. al. [3] reported that when cement contain considerable amount of vitreous blast furnace slag (either granulated or pelleted) their cementitious derived products exhibit good durability. Such statements, however still require further study.

Cement containing alkali-activated-slag was first developed in the early 60's by Glukhovsky and Wang [4]. Recently, Escalante et. al. [5] analyzed the hydration products and the reactivity of blast furnace slag using $Na_2{\cdot}nSiO_2$, NaOH and carbonates admixtures, sulfates and hydroxides as chemical activators. These later studies confirmed that the major hydration product formed when analyzing several activating agents is calcium silicate hydrate (CSH). X-ray studies conducted on such material revealed the presence of a hydrated calcite phase, suggesting that the addition of NaOH makes slag more reactive. Irassar [6] on the hand replaced cement by granulated blast furnace slag to improve its mechanical resistance and determined that its strength depends on the amount of slag. Locher [7] concluded that the ultimate strength of concrete containing slag is a function of the microstructure of constitutive particles. Mejia et. al. [8] conducted a study based on the sulfate attack to a material made out of a mixture of activated slag and Portland cement. They reported stability of their specimens to sulfates and attributed major resistant to sulfate attack due to the alkali-activated slag as compared to those made by Portland cement with no slag. From the work of Kurtis [9] it can be inferred that given the mechanical advantages conferred to cement through the proper addition of blast furnace slag (such as high compressive strength, high resistance to chemical attack and low synthesis temperature), this kind of material is potentially more convenient than normal ordinary Portland cement.

This work aims to study the durability of some blast furnace slag-based cements and H-class cementitious composites (which are suitable for applications such as cementing in oil wells), throughout their compressive strength evaluation and chemical attack to sulfates, as well as analyzing their general behavior when exposed to alkalis.

Materials and methods

The cementitious materials used are: granulated blast furnace slag (GBFS) and H-class cement. The GBFS is a glassy slag provided by the Altos Hornos de Mexico Company and has a specific gravity of 2960 Kgm^{-3}. Its chemical composition is presented in *Table 1.*, including the H-class cement. Because of its hydraulic characteristics, grain size and high resistance; this cement is used in practice for protection from chemical attack to sulfates. The chemical agent used in the preparation of studied material is an alkaline solution of sodium hydroxide (NaOH) at concentrations of 2 and 5% in relation to the mass of slag. This research has been conducting in accordance to the methods established under Mexican standards for assessing the technical suitability in developing an alternative cementitious product. Mexican standards followed in this work include NMX C 418 ONNCCE 2001, which relates to the ASTM C-1012. For the microscopic analysis conducted in this work a scanning electron microscope (JEOL 6360LV) was used.

Granulated blast furnace slag (GBFS)		Class-H cement	
Compound	Composition (%)	Compound	Composition (%)
CaO	35.70	CaO	64.80
SiO_2	36.90	SiO_2	20.61
Al_2O_3	9.41	Al_2O_3	3.27
Fe_2O_3	2.28	Fe_2O_3	5.31
MgO	9.03	MgO	1.95
SO_3	0.06	-	-
S-	1.60	-	-
Na_2O	1.10	Na_2O	0.51
K_2O	1.20	K_2O	0.21
R.I.	0.19	R.I.	0.21
R.F.	2.49	R.F.	1.22

Table 1. Chemical composition of materials used in this work (weight %)
1. táblázat A vizsgált anyagok kémiai összetétele (tömeg %)

The chemical formulation of the specimens used in the compressive strength and sulfate testing is described in *Table 2*. The compositions of the materials used in the reactivity test to aggregate alkali are also listed. For each of the composites shown in Table 2., nine cubes of 50 mm side and six bars of 250 × 25 × 25 mm were prepared (MNX C 061 ONNCCE 2001). The cement cubes were used to measure compressive strength in a hydraulic commercial machine, (Soilest Model CI-7510). The bars were immersed in sulfate solutions at setting times of 1, 3, 7, 14 and 28 days. The longitudinal change occurred in the samples before and after the endurance of sulfate resistance test was carried out using a commercial digital display (Humboldt MFG CO H model 3259).

For compressive strength and sulfate resistance	For reactivity to aggregate alkalis
100 % H-cement	100 % H-cement
100 % GBFS activated with 2% NaOH	
100 % GBFS activated with 5% NaOH	100 % GBFS activated with 5% NaOH
80 % GBFS – 20% H-cement	
60 % GBFS – 40% H-cement	
40 % GBFS – 60% H-cement	40 % GBFS – 60% H-cement
20 % GBFS – 80% H-cement	20 % GBFS – 80% H-cement

Table 2. Formulation of materials used to evaluate the compressive strength and sulfate resistance, as well as proof of reactivity to aggregate alkalis (wt %)
2. táblázat A nyomószilárdság és a szulfátállóság, valamint az aggregátumok lúggal szembeni viselkedésének vizsgálatához használt anyagok összetétele (tömeg %)

Results and discussion

Compressive strength

Fig. 1. shows the compressive strength of the cementitious composites analyzed. These include H-class cement and that of the activated slag with 2 and 5% NaOH as a function of setting time. The cementitious composites developed their compressive strength much slower than that shown by the H-class cement at initial stages (3–7 days), which according to Barnett [10] is a feature of cements having high slag content (<50% of GBFS). The addition of GBFS to H-class cement undermines the compressive strength as compared to its pure state, although it tends to improve along further setting time. For pure H-cement this parameter tends to increase over the first 7 days of curing. Note that both the pure H-class cement (─▲─) and the composite 20% GBFS - H-cement (─►─) provide mechanical resistance to compression above 20 MPa at 7 and 14 days, respectively. For GBFS at 100% without NaOH it would not be possible to assess the resistance because it does not cure its own without the presence of sodium hydroxide or other alkali. In the case of GBFS, which was NaOH-activated it is observed that the compressive strength increases as the alkali concentration is higher. In both cases, resistance tends to increase up to 14 days to develop very shortly thereafter. This is attributed to the fact that NaOH acts as a cement retardant, in addition to the activators that disclose a specific selectivity [11], which in turn depends on the used materials chemical composition. Studies carried out by different researchers [6–8] report that activated slag cements are basically dependent on the same factors as ordinary Portland cement, although in

the first case the initial reaction mechanisms are dissolution and precipitation [3]; whereas in the case of ordinary Portland cement it is attributed to more than a diffusion phenomenon. The large compressive strength observed at early setting times on those cementitious composites is associated to the nature of the anion present in the activating solution. In this case, the presence of Na^{+} cations, which initially compete and/or interact with the Ca^{++} cations in the slag form the calcium silicate hydrate (CSH gel) responsible for the development of resistance [3].

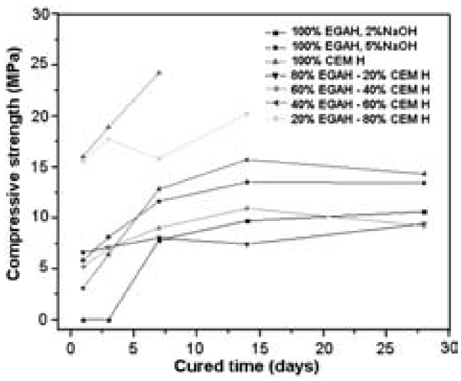

Fig. 1. Compressive strength observed in different cementitious composites
1. ábra A különféle kísérleti cementek nyomószilárdsága

Durability of cementitious composites to chemical attack

A. In Magnesium sulfate solution ($MgSO_4$)

Since $MgSO_4$ tends to react with the mineral constituents of cement by creating product compounds whose crystalline volume per unit cell is larger than its precursors, the mechanical resistance of cementitious composites was determined throughout evaluation of their expansion percentage shown when exposed to sulfates. Macroscopically, those materials reveal volumetric expansion by swelling themselves; this could lead to catastrophic fracture of the cementitious composites. This failure risk can be prevented if the evaluation approach reveals that the value of the expansion is minimal. The results are shown in *Fig. 2. (a) and (b).* It is noted that the increase in the amount of slag in H-class cement reduces the percentage of expansion from 0.07% to 0.02% after 12 months. *Fig. 2. (a)* shows that compared to the composites exposed to the same conditions, pure H-class cement undergoes larger expansion level despite being a cement composite designed to withstand aggressive chemical reactions. Cementitious composites with composition of 60% H CEM GBFS -40% (—▲—), 40% H CEM GBFS -60% (—▼—) and 20% H CEM GBFS -80% (—◆—) have a similar expansion behavior, which is much lower than that of pure H-class cement. Therefore, one would expect these materials to disclose an adequate resistance to sulfates. In general, these results show that when GBFS is activated with NaOH it triggers resistance, which increases up to 28 days. This indicates that the addition of slag improves the composites resistance to chemical attack. The materials that reached 20 MPa before the 28 days, such as 100% H CEM and 20% GBFS -80% CEM H experience greater expansion than those which did not reach it, as it is the case of 100% activated GBFS 5% NaOH.

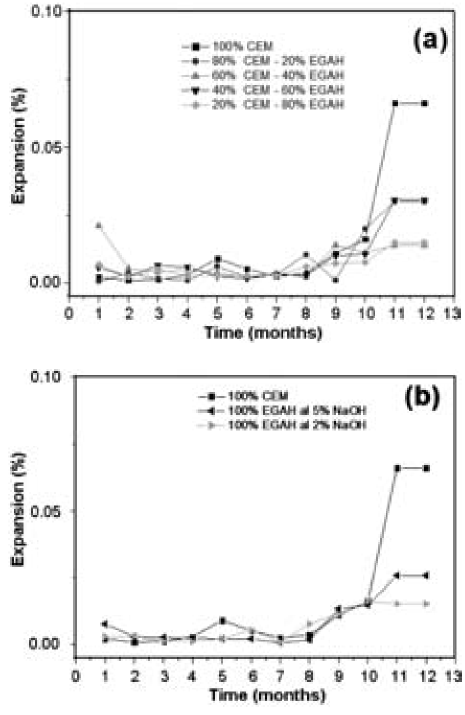

Fig. 2. (a) Volumetric expansion behavior shown by cementitious composites and CEM-H in magnesium sulfate $MgSO_4$, (b) H-CEM and GBFS behavior activated with 2 and 5% NaOH
2. ábra (a) a különféle kísérleti cementek és a CEM-H térfogatának növekedése magnézium-szulfát oldatban, (b) a 2, illetve 5% NaOH-dal aktivált granulált kohósalak és a CEM-H viselkedése

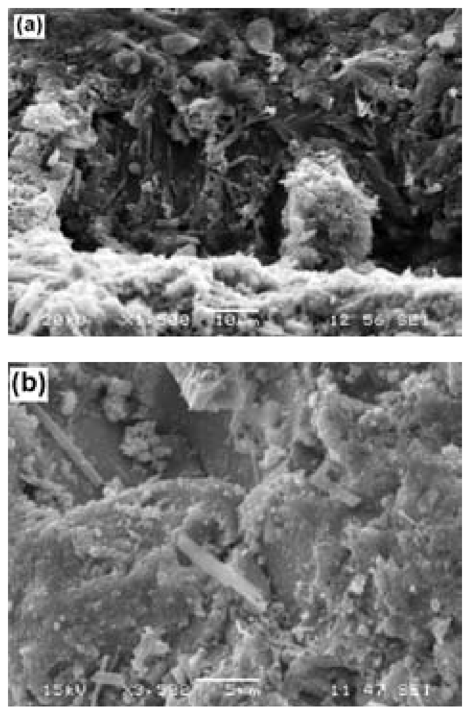

Fig. 3. Micrograph of the H-class cement, (a) showing a pore and (b) a deposition of ettringite in the pore
3. ábra A CEM-H SEM felvétele (a) egy pórus képe, (b) ettringit lerakódása a pórusban

Derived from the scanning electron microscopy (SEM) analysis, it was confirmed the formation of some products resulting from the interaction between the blast furnace slag-based composites cementitious and the H-class cement in the magnesium sulfate solution. *Fig. 3. (a)* shows a micrograph of H-class cement revealing the pores present, which when observed at higher magnification (*Fig. 3. (b)*), are found to be filled with needle-shaped crystals, corresponding to ettringite.

B. In sodium sulfate solution (Na_2SO_4)

Fig. 4. (a) and (b) show the volume expansion percentage of studied material monitored for one year along its exposure to this environment. Initially, the edges found on the surface of specimens enlarged through a sort of peeling process occurred at the top and bottom of the bar-samples. For some bars it was even noticed that the expansion process took place whereas the addition of larger amounts of slag reduces the expansion percentage to values below 0.1% after 12 months. It is noteworthy that sodium sulfate is a much more aggressive agent than magnesium sulfate. Thus, the H-class cement slowly increases the rate of expansion. After nine months testing the volume expansion of analyzed material starts to rise in all cases. Such subsequent behavior is associated to the precipitation of sulfates, basically occurred in the center of the grains without causing any cracking. The later is based on the fact that no composite expansion was recorded to exceed the limits set out in NMX C 418 ONNCCE 2001, which is of 0.07% at maximum. Moreover, according to the American norm ASTM C-1012 used in several investigations [6, 12–13] the maximum volume expansion allowed in these specimens is of 0.05% during the first 6 months. If the later takes place in the analysis then such material having high resistance to sulfates and 0.10% expansion can be classified as one of moderate resistance. The expansion percentages obtained in this investigation indicate that the slag activated with sodium hydroxide corresponds to a material with high resistance to sulfates.

The scanning electron microscopy SEM study confirmed the formation of some products resulting from the interaction between the blast furnace slag-based cementitious composites and H-class cement in the sodium sulfate solution. *Fig. 5. (a)* shows the surface of the H-class cement showing a particle size of 10 μ m. Although in this case, it was not observed the presence of pores or cracks. *Fig. 5. (b)* shows the formation of gypsum and ettringite crystals.

C. Alkali aggregate reactivity

The alkalis (Na^+ and K^+) are typically encountered in the Portland cement chemical composition, although other major cations may additionally be supplied through the incorporation of enriching materials. Granulated blast furnace slag GBFS substantially increases the amount of Si^{2+}, Ca^{2+} and Al^{+3} through a past richer in SiO_2, CaO and Al_2O_3 (see Table 1). Thus, ions might undergo reactive with specific aggregates (quartz, chalcedony, opal, volcanic glass, clay, etc.) modifying acidic and/or basic behavior of cement and thus its final properties. To assess the chemical reactivity of alkali aggregates in the studied cement and aggregate admixtures it was analyzed the potentially expansive reactions, involving hydroxide ions that are associated to (sodium and potassium) alkalis by measuring the length of the cement bar. *Fig. 6.* shows the volume expansion percentage, which indirectly reflects the reaction effect between the alkali in the solution and reactive aggregates (Pyrex glass). The volume expansion was measured directly from the mortar bars at 38 °C ± 2 °C and a relative humidity of not less than 80%.

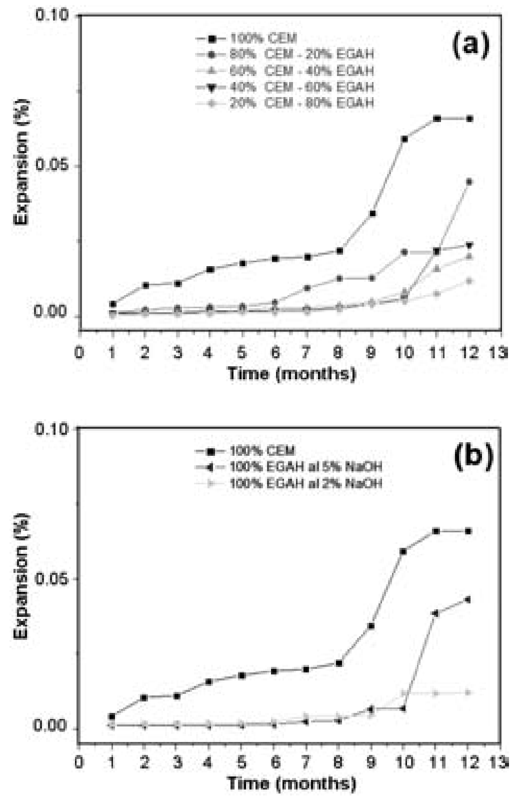

Fig. 4. Volume expansion behavior of blast furnace slag-based cementitious composites exposed to Na_2SO_4

4. ábra A kohósalakot tartalmazó különféle cementkompozíciók térfogat növekedése Na_2SO_4 oldatban

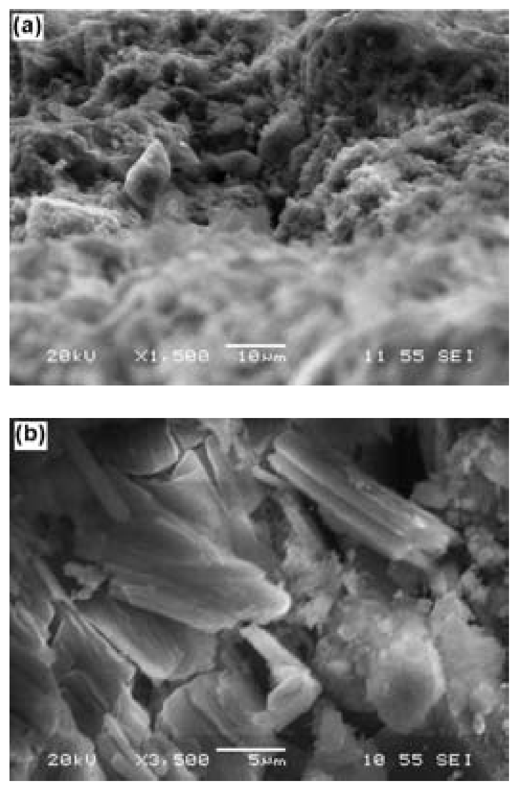

Fig. 5. (a) Micrograph of the surface of the H-class cement and (b) magnification of formed crystals

5. ábra (a) a CEM-H felületéről készített SEM felvétel, (b) a képződött kristályok kinagyítva

The reaction most often occurred between alkalis and silica, takes place between alkali cement and aggregates. The reaction products can be represented in simplified form as follows:

$$SiO_2 + 2NaOH + H_2O \rightarrow Na_2SiO_3 \cdot 2H_2O$$

The gel product of the reaction has the ability to absorb water and therefore increases in volume. This expansion creates internal tensile forces that end up breaking the mortar. Therefore, it appears that both the H-class cement, as well as the 5% NaOH alkali activated GBFS and the 80% cement composite H-20% can be considered as materials with a moderate alkali aggregate reactivity. That explains why no cracks or fissures are observed in the petrographic inspection (i.e., given the slowness of the reaction).

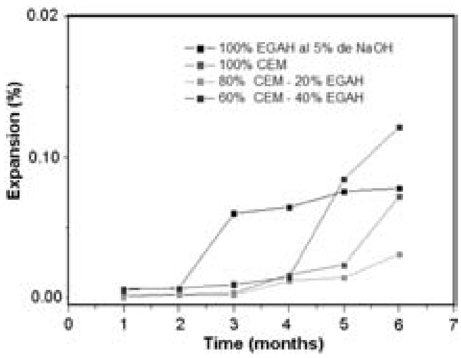

Fig. 6. Mean volumetric expansion of cementitious composites testing aggregate alkali reactivity

6. ábra A különféle cementkompozíciók átlagos térfogat növekedése az aggregátumok lúgokkal szembeni viselkedésének vizsgálatakor

Conclusions

- The durability effect of H-class cement, considered suitable for cementing oil wells, was evaluated in this study by mixing it with blast furnace slag and its activation with NaOH.
- A limited durability of the cementitious composites is inferred from axial-compressive testing. The compressive resistance of composites decreases as the percentage of slag rose.
- The addition of 60 and 80wt% slag reduces the volume expansion level to values below 0.1% after 12 months testing.
- The volume expansion level of the H-class cement specimens after being activated with NaOH reduced as the granulated blast furnace slag GBFS amount was increased.
- Since the cementitious composites obtained after 12 months disclosed a volume expansion of about 0.035%, they can be considered as materials of moderate resistance to sulfate.
- The main reaction products detected in cementitious composites are hydrated calcium silicate, ettringite, gypsum and small amounts of hydrotalcite.

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H-osztályú cement és nagyolvasztói salak alapú kompozit cementek tartóssága

Az acélgyártási salakok újszerű cementekben, vagy különleges cement kompozíciókban történő felhasználását mind környezetvédelmi, mind gazdasági szempontból már széleskörűen vizsgálták. Ugyanakkor a granulált kohósalakok (GBFS) esetében még kutatásokra van szükség annak felderítésére, hogy azok bekeverése miként befolyásolja a cementek tartósságát. Cikkünkben egy olyan, olajkutak bélelésére használt H-osztályú cement tartósságát vizsgáljuk, amelyhez kohósalakot adagoltunk, majd NaOH-dal aktiváltunk. Kutatásainkat az alternatív cementtermékek kifejlesztésének műszaki szempontjaira vonatkozó mexikói szabványok szerint végeztük. Meghatároztuk a kapott termékek kémiai összetételét, nyomószilárdságát, és szulfátállóságát. Mikroszerkezetüket pásztázó elektronmikroszkópos felvételek alapján jellemeztük. Eredményeink szerint a cement kompozíciók mérsékelten tartósak: mechanikai sajátságaik a salaktartalom növelésével romlanak, és szulfátállóságuk sem megfelelő. A salaktartalom növelésével ugyanakkor a cement duzzadóképessége csökkent.

Kulcsszavak: cementkeverékek, aggregált, lúggal kezelt kohósalak, tartósság, szulfátállóság