Long-term strength and resistance to chemical aggressive environments of blast furnace slag, pozzolan and limestone ternary cements

Resistência a longo prazo e resistência a ambientes químicos agressivos de cimentos ternários de escória de alto-forno, pozolana e calcário

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ABSTRACT

In the cement industry, the search for a less expensive binder using mineral additions from industrial by-products or natural resources has become a major concern on the one hand to compensate for the deficit in the manufacture of Portland cement and on the other hand to reduce the environmental impact linked to the massive use of Portland cement. This research aims studying the feasibility to produce ternary cement systems by replacing clinker with a binary combination of two different mineral additions. Two types of ternary cement systems were studied: type A with 65% clinker and 35% (natural pozzolan and limestone), and type B with 65% clinker and 35% (blast furnace slag and limestone), were the combination of mineral additions was 10%+25%, 17,5%+17,5%, and 25%+10%, respectively. Study of mortars (type A or B, and sand) compressive strength at the ages of 28 days, 1 year and 3 years was carried on. Resistance to chemical aggressive environments, namely sulphuric acid (H_2SO_4) and hydrochloric acid (HCl) solutions, was also studied after an initial 28 days curing and for six months period of immersion, by compressive strength test, weight and pH changes. The effect of aggressive environment on the internal microstructure was also studied by mercury intrusion porosimetry (MIP).

Keywords: cements, slag, pozzolan, limestone, strength, acid.

RESUMO

No setor de cimento, a busca por um aglutinante mais barato usando adições minerais de subprodutos industriais ou recursos naturais tornou-se uma grande preocupação, por um lado, para compensar o déficit na fabricação de cimento Portland e, por outro lado, para reduzir o impacto ambiental ligado ao uso maciço de cimento Portland. O objetivo desta pesquisa é estudar a viabilidade de produzir sistemas de cimento ternário substituindo o clínquer por uma combinação binária de duas adições minerais diferentes. Foram estudados dois tipos de sistemas ternários de cimento: o tipo A, com 65% de clínquer e 35% (pozolana natural e calcário), e o tipo B, com 65% de clínquer e 35% (escória de alto-forno e calcário), em que a combinação de adições minerais foi de 10%+25%, 17,5%+17,5% e 25%+10%, respectivamente. Foi realizado o estudo da resistência à compressão das argamassas (tipo A ou B e areia) nas idades de 28 dias, 1 ano e 3 anos. A resistência a ambientes quimicamente agressivos, a saber, soluções de ácido sulfúrico (H2SO4) e ácido clorídrico (HCl), também foi estudada após uma cura inicial de 28 dias e por um período de seis meses de imersão, por meio de teste de resistência à compressão, alterações de peso e pH. O efeito do ambiente agressivo na microestrutura interna também foi estudado por porosimetria de intrusão de mercúrio (MIP).

Palavras-chave: cimentos, escória, pozolana, calcário, resistência, ácido.

1 INTRODUCTION

Greenhouse gases (GHG) emissions and waste from sources across a spectrum of industrial processes pose negative impacts on human health and the environment. Climate change associated with GHG emissions is one of the most pressing concerns facing the planet. In 2012 Algerian GHG emissions totalled 153 MT CO_2-equivalents and growing at a rate of over 3% despite the contribution of Algeria on global warming is minimal (less than 0.5% of global GHG emissions) (Sahnoune *et al*., 2016).

Global CO_2 emissions mainly reflect the world’s fossil energy consumption, including oil and gas production, cement and steel construction. The impact of the production of Portland cement on CO_2 emissions is recognized worldwide today. Cement production accounts for roughly 8% of global CO_2 emissions. Both non-combustion and combustion emissions from cement production occur during the clinker production process. About half of CO_2 emissions are generated by carbonate oxidation in the cement clinker production process, the main constituent of cement and the largest of non-combustion sources of CO_2 from industrial manufacturing, and the other half is generated by fuel combustion emissions related to cement production (Olivier *et al*., 2015).

Thus, a growing number of studies are being undertaken to develop binders with reduced environmental impact. One of the paths explored involves substituting a substantial portion of the clinker with mineral additives from industrial by-products (e.g. blast furnace slag or fly ash) (Csagnabèe *et al*., 2011). These additional ingredients can help improve the performance of long-term concrete. However, the widespread use of these mineral additions in cements, replacing clinker, usually results in a significant decrease in the kinetics of cure and performance of the material at the young age. One way to counteract these phenomena on early ages is by adding limestone combined either with pozzolan or blast furnace slag. The cement matrices made up with ternary binders have showed higher performance than binary based binder matrices in terms of heat generation, mechanical strength at early age and as well durability related properties (Menéndez *et al*., 2003). The beneficial effect of limestone fillers on the hydration rate of the cement Portland at the young age has already been demonstrated in previous studies (Lothenach *et al*., 2008; Bouasker *et al*., 2008; Mounanga *et al*., 2010; and Khalifa *et al*., 2013). The limestone filler improves the arrangement of hydrates within hydration current matrices and also increases the number of nucleation sites for the development of hydrates (Gomes *et al*., 1997).

This research aims to study long-term compressive strength and resistance to aggressive solutions by measuring weight, porosity and compressive strength changes of ternary cement systems with less clinker content by replacing it by a binary combination of two different mineral additions. Two types of different ternary cement systems (clinker + mineral additions) were studied: type A (natural pozzolan + limestone), and type B with (blast furnace slag + limestone), were the combination of mineral additions was 10%+25%, 17,5%+17,5%, and 25%+10%, respectively. The long-term study of strength development and resistance to chemical aggressive environments, of mortars (type A or B + sand) was carried on at the ages of 28 days, 1 year and 3 years.

2 EXPERIMENTAL

2.1 MATERIALS

The clinker used in this research was obtained from cement plant of Ain Kebira Company (Setif, region– East of Algeria). The chemical and mineralogical composition of clinker is given in Tables 1. and 2, respectively. The clinker was mixed with 3% gypsum and each mineral addition was grounded separately in a laboratory ball mill. The Blaine fineness of clinker and additions obtained was 3500 ± 100 $cm^2.g^{-1}$. Densities of clinker, limestone, slag and natural pozzolan are of 3.2, 2.7, 2.65 and 2.8 $g.cm^{-3}$, respectively. The chemical composition of mineral additions is also presented in Table 1. The gypsum used in this study is a natural addition delivered from the deposit of Djemila (East of Algeria). The limestone was obtained from quarry of Ouled Eddouene, near Ain Kebira (region of Sétif). Such type of limestone as being widely used since it is considered as an inert natural addition. The Pozzolan used is a natural pozzolan obtained from Bouhmidi deposit (Beni Saf), located about 20km distance of coast and it was provided by Zahana cement Company.

The blast furnace slag is a by-product of iron ore processing obtained from plant for steel manufacturing located in Annaba (North-East Algeria) (Kellouche *et al*., 2010; Zeghichi *et al*., 2005). Its chemical composition is also presented in Table 1.

The sand used is a standardized river sand size range 0-2 mm, according to the French standard AFNOR (NFP 15 – 403., 1996). The water used is tap water supplied by water public service.

Table 1. Chemical composition of clinker and mineral additions (%)

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	SO_3	TiO_2	L.O.I
Clinker	63.73	21.42	4.58	4.96	1.43	-	0.24	0.72	-	2.94
Gypsum	22.5	3.8	0.5	0.1	0.58	-	-	32.84	-	39.09
Limestone	45.85	12.74	1.65	0.58	0.73	-	-	-	-	37.54
Slag	47.13	32.90	9.42	0.93	4.11	0.81	0.39	1.30	0.66	-
Pozzolan	13.20	43.41	20.45	9.60	4.77	1.54	4.09	-	2.23	-

Clinker supplied by cement plant of Ain El Kebira Company; **Gypsum** delivered from the Djemila deposit East of Algeria. **Limestone** obtained from quarry of Ouled Eddouene. **Pozzolan** obtained from Bouhmidi deposit (Beni Saf)

Source: Authors

2.2 SPECIMENS FOR TESTING

Two types of ternary cement mortars (clinker + mineral additions + sand) were prepared, the mass and chemical composition of mixed raw materials used in mortars is given in Tables 2 and 3, respectively. The binder/sand (b/s) volume ratio was 1:3 for all specimens. The percentage of clinker replacement was made by mass. The mortar water/binder (w/b) ratio was kept constant at the 0.5. Mortars were mixed according to the EN 196-1 standard and 40 x 40 x 160 mm^3 prisms were produced. After casting, the mortar specimens were cured in mould for 24 hours inside a controlled curing room at 20 ± 2°C and constant relative humidity about 80%. Afterwards specimens were removed from moulds and cured in water up to 28 days. For each type of cement system and combination of mineral additions 65 mortar specimens were produced in a total of 130. Part of specimens was used for long-term compressive strength development (total of 75) and the other part (45) was used for the study of the resistance to aggressive solutions.

Table 2. Mass composition of the cementitious systems (%). Type A: 65% Clinker + 35% (natural pozzolan + limestone), Type B: 65% Clinker + 35% (blast furnace slag + limestone)

Type	Mix	Clinker	Gypsum	Limestone	Pozzolan	Slag
A	A1	62	03	25.0	10.0	-
	A2	62	03	17.5	17.5	-
	A3	62	03	10.0	25.0	-
B	B1	62	03	25.0	-	10.0
	B2	62	03	17.5	-	17.5
	B3	62	03	10.0	-	25.0

Source: Authors

Table 3. Chemical composition of mixed raw materials (%).

Type	Mix	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	SO	L.O.I
A	A1	60.60	35.22	1.82	1.31	0.31	-	-	0.7	0.0
	A2	49.97	38.73	4.71	2.73	1.48	-	0.68	1.4	0.1
	A3	46.29	40.11	5.95	2.39	1.85	-	1.36	2	001
B	B1	28.03	64.74	2.97	1.81	0.73	-	0.42	0.74	-
	B2	48.62	42.04	3.64	2.07	1.58	0.34	0.59	0.93	-
	B3	59.18	28.94	4.84	2.50	1.83	0.49	0.89	0.99	0.34

Source: Authors

2.3 METHODS

After the initial period of 28 days curing in water, part of type A and B specimens were immersed in two different aggressive chemical environments, namely 3.5% sulphuric acid solution (H_2SO_4) and 5% HCl solution, for six months' immersion period. All solutions were kept at a temperature of about 22ºC. Specimens of different types were kept immersed in separate tank solutions.

Weight changes of specimens were made after 56 days and 6 months immersion period. Weight measurement and compressive strength test was carried on before and after 6 months' immersion.

Before each test the specimens were washed with water follow by drying in laboratory conditions (20ºC, 60% RH) for 3 hours. The pH value of specimens was also determined before and after 6 months immersion. The method to obtain pH consisted of mixing powder of external surface of specimens with a solvent and measuring the pH of the suspension. The pH determination was carried on by pH electrode HANNA HI 4221 equipment.

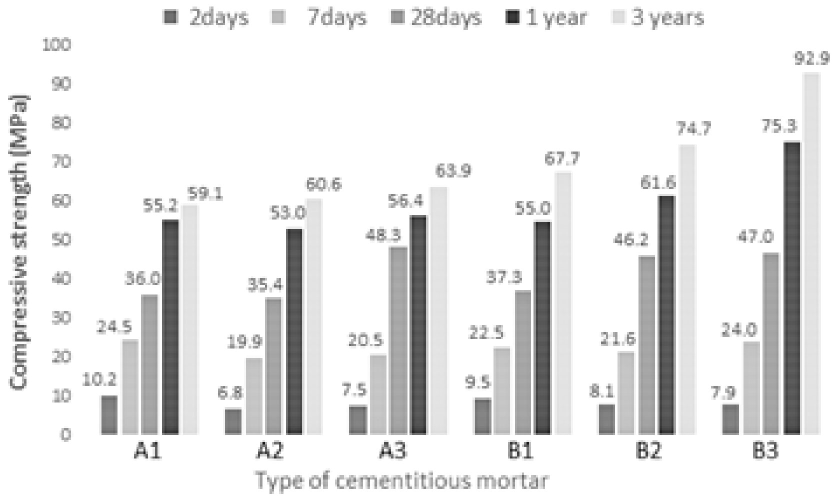
Additionally, part of A and B type specimens were left to cure immersed in water for 3 years, for long-term strength development study. Compressive strength tests were carried on 2, 7 and 28 days, 1 and 3 years age. Changes on porosity were determined by microporosimetry mercury intrusion (MIP) AutoPore IV equipment. Samples to be tested by SEM, XRD and MIP were dried in oven for 24 hours.

3 RESULTS AND DISCUSSION

3.1 LONG-TERM COMPRESSIVE STRENGTH

Figure 1 shows the development of long-term compressive strength for different cement systems, up to 3 years of curing.

Figure 1. Long-term compressive strength.



Type A: 65% Clinker + 35% (natural pozzolan + limestone), Type B: 65% Clinker + 35% (blast furnace slag + limestone)
Source: Authors

The figures show that the strengths of mortars containing blast furnace slag achieved highest compressive strength in all cases than those made with natural pozzolan. Also, it was verified that increasing the blast furnace slag content gives a higher increase in compressive than in case of mortars made with natural pozzolan. Thus, the highest compressive strength was found on B3 type mortars were the combination of mineral additions was 10% Limestone and 25% Blast furnace slag. In opposition the lowest compressive strength was found on A1 type mortars with 25% Limestone and 10% natural pozzolan. It can also be found that the compressive strength of mortars A1 and A2, respectively with 25% limestone and 10% natural pozzolan and 17.5% Limestone and natural pozzolan is of the same order of magnitude. As well, the compressive strength achieved by mortar types A3 and B1 after 3 years curing, containing respectively 10% limestone and 25% natural pozzolan, and 25% limestone and 10% blast furnace slag, is also of similar value. While, both mortars B2 and B3, respectively with 17.5% limestone and blast furnace slag, and 10% limestone and 25% slag, present the highest compressive strength values, and the highest compressive strength of about 93 Mpa was found on B3 type mortars after long-term curing.

However, it should be noted that relative differences in compressive strength development only emerge after 28 days of curing, after long-term curing. At short-term study, namely at 28 days, most mortar types have achieved identically compressive strength results where mortar type A3 containing 10% limestone and 25% natural pozzolan shows slightly highest results than all the rest. But the relative differences of increase in strength become more important in long-term study. Also, it has been show by other authors that both natural pozzolan and blast furnace slag used in this study have a beneficial pozzolanic effect in compressive strength development as substitutes of clinker (Menéndez *et al*., 2003). In the case studied this benefit is also confirmed. Additionally, it was verified that such natural pozzolan increases the compressive strength that early-ages, up to 28 days, while blast furnace slag contributes for strength development at long-term, from one to three years curing.

3.2 EFFECT OF POZZOLAN AND SLAG IN COMPRESSIVE STRENGTH

As presented earlier Figure 1 depicts the long-term compressive strength for both A and B cement systems. It is clear that the compressive strength increases continuously along time of curing for all different mortars, however the development of compressive strength of both cement systems does not occur in the same manner. Type A natural pozzolan cement systems showed an increase in compressive strength at early-age sup to 28 days, while type B blast furnace slag cement systems contributed for higher strength development at long-term. In both A and B cement system mortars containing higher percentage of limestone showed an increase of compressive strength at early ages (2 days) when compared to the strength gain at 07 days and later. Thus the strength gains of different cements is dependent on the kinetics of hydration and in particularly on the pozzolanic effect of each cement system.

In fact, long-term compressive strength of mortars made from blended cement with mineral additions such as slag and pozzolan is largely influenced by the amount of C–S–H formed during the hydration of cement. In general, the pozzolanicity of the mineral admixture influences the rate of hydration. For example, in case of limestone the lower long-term strength development is attributed to its lower reactivity (Benkaddour *et al*., 2013). Thus, in this study, higher long-term strength development of B type cement systems can be attributed to the later pozzolanic activity of the blast furnace slag. In turn natural pozzolan might contribute for fixing portlandite $Ca(OH)_2$ and limestone which will also cause new calcium silicate hydrates (C–S–H) to be formed that will participate in the development of strength at later stages but in this case in lower increase.

However, limestone in Portland cement as a replacement of clinker leads to a rise in short-term strength, whereas slag and pozzolan lead to a decrease. The addition of $CaCO_3$ to the C_3S accelerates the hydration of cement at early ages and modifies the Ca/Si ratio of calcium silicate hydrates (C–S–H). These last studies confirm the significant effect of limestone fillers on the hydration of cement at early age (Beddoe *et al*., 2005; Larreur-Cayol *et al*., 2011; Alexander *et al*., 2013 and Gutberlet *et al*., 2015). While, at long-term, cements with pozzolanic materials and especially blast furnace slag exhibit significantly higher compressive strength than the Portland cement and the Portland-limestone cement (Kadri *et al*., 2009). Blast furnace slag can provide additional aluminates which will lower the sulphate/aluminate ratio and thereby amplify the impact of the limestone. Thus, part of aluminates liberated is incorporated in the C-S-H gel as observed by the increase of the Al/Si ratio of the C-S-H phase (Ghrici *et al*., 2007 and Isaia *et al*., 2003).

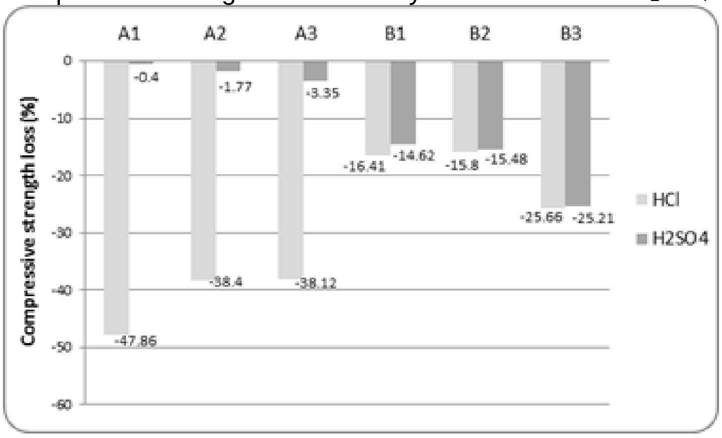
Thus, the synergic interaction between limestone and blast furnace slag, limestone and natural pozzolan and its influence over time was confirmed by the long-term compressive strength development. Natural pozzolan interacts with the hydration phases, leads to the formation of mono or hemicarboaluminate hydrates. Blast furnace slag hydrates by itself and stabilizes thereby the ettringite. This last leads to an increase in the volume of hydrates and a subsequent decrease in porosity and a higher increase in strength development.

3.3 CHANGES OF COMPRESSIVE STRENGTH AFTER IMMERSION IN AGGRESSIVE SOLUTIONS

3.3.1 Effect of sulphuric acid solution (H_2SO_4)

Figure 2. shows the loss of compressive strength of mortars exposed to sulphuric acid solution after 56 days of immersion.

Figure 2. Loss of compressive strength after 180 days of immersion in H_2SO_4 and HCl solutions



Source: Authors

Mortars containing cement system with natural pozzolan and limestone (type A) showed only a small decrease in compressive strength after immersion while type B mortars containing blast furnace slag presented a higher decrease in strength. In particularly, type B3 specimens containing the highest percentage of blast furnace slag showed a decrease in strength (about 25.7 %). The results obtained are in accordance with loss of weight of specimens after immersion in H_2SO_4 solution as discussed earlier.

3.3.2 Effect of hydrochloric acid (HCl)

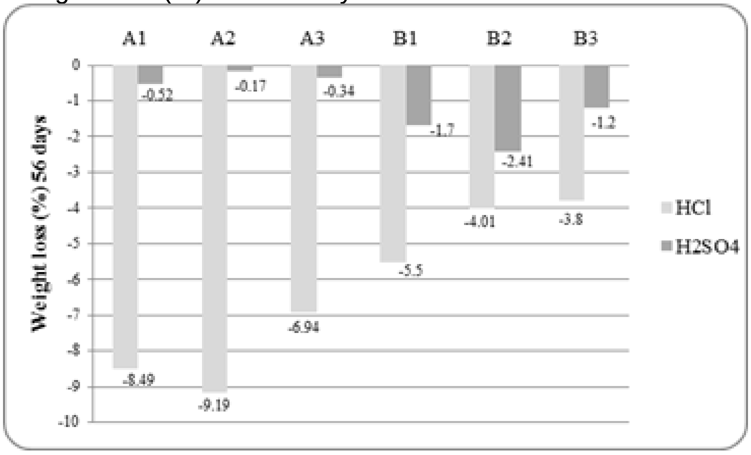
Figure 2 also shows the loss of compressive strength after 180 days of immersion in hydrochloric acid solution. Type A cement system (with pozzolan and limestone) showed significant decrease in compressive strength, while on type B cement system (with blast furnace slag and limestone) the strength shows less decreased. All type B mortar samples show a less decrease in compressive strength compared to those of the type A. In particularly A1 specimens containing 10% of pozzolan and 25% of limestone presented the highest decreased in compressive strength of about 47.9 %. Again, the results obtained are in accordance with loss of weight of specimens after immersion in HCl solution.

3.4 RESISTANCE TO AGGRESSIVE SOLUTIONS

3.4.1 Degradation in sulphuric acid (H_2SO_4)

The specimen weight changes results resulting of exposure in H_2SO_4 and HCl solutions for 56 and 180 days period of immersion are shown in Figs. 2 and 3. respectively. Exact values can be obtained from Tables 4 and 5.

Figure 3. Weight Loss (%) after 56 days of immersion in H_2SO_4 and HCl solutions



Source: Authors

The results show that up to 56 days immersion period in H_2SO_4 solution the decrease in weight is relatively low in both type A and B specimens. During the 56 days of immersion type A specimen's weight loss is between 0.1 to 0.5% while in type B specimens is between 1.2 to 2.4%. However, after 56 days immersion in H_2SO_4 solution the decrease in weight is very significant in both type specimens, particularly type B specimens produced with the cement system containing blast furnace slag (approximately 10 to 14% loss of weight). While, type A specimens show lesser decrease in weight loss for the same immersion conditions and period (varying in this case from about 4 to 8%).

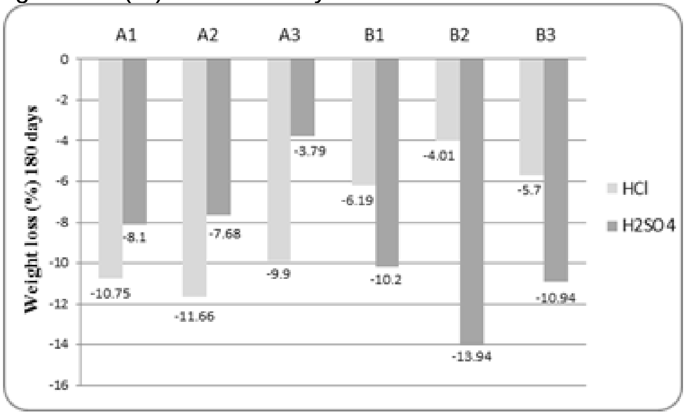
The reaction of cement mortar with sulphuric acid (H_2SO_4) is well known. Essentially, calcium hydroxide reacts with the sulphuric acid to form calcium sulphate, which is deposited as gypsum. Gypsum resulting of calcium hydroxide reaction with the sulphuric acid is easily leached resulting in considerable weight loss. As the reaction proceeds, all the components of the cement can be decomposed and leached away. In addition, the calcium sulphate consisting of first reaction may react with the calcium aluminate phase present in the cement to form sulfoaluminate and hydrated calcium (ettringite), which after crystallization, may cause the expansion of the mortar. As reported by other authors in cements with additions, such is the case in study, the amount of calcium hydroxide (CH) is significantly smaller than in the cement without the addition, this is because the pozzolanic reaction fixes lime (CH). Therefore, the capillary pores are reduced by formation of the CSH gels and blocking the absorption of the acid solution, resulting in a reduction of weight loss (Radlinski *et al*., 2012).

In the case of this study, a significant weight loss was found in both type A and B mortars after being immersed in H_2SO_4 solution for 180 days. Expansion of mortars was not detected. So, the weight loss can be attributed to the reaction of sulphate ions (SO_4) with CH, leading to the formation of gypsum that was, in turn, leached away from samples, particularly after 180 days immersion, as was confirmed by the whitening out showing at the outer surface of mortar samples before measurements. From this study we can also assume that the pozzolanic reaction of calcium hydroxide was better developed in mortars produced with natural pozzolan (type A) since those suffered less weight loss during immersion in H_2SO_4 solution in comparison with the ones produced with blast furnace slag (type B). Mortar A3 containing 25% natural pozzolan and 10% limestone addition shows the lowest weight loss, which might be explained by a better-developed pozzolanic reaction; i.e. a lowest amount of crystal CH available to react with sulphate ions (SO_4).In the case of mortars produced with limestone and blast furnace slag the amount of crystalline CH available in the hydrated samples may be somewhat higher and thus the reaction with the sulphate ions was larger, resulting in higher weight loss.

3.4.2 Degradation in hydrochloric acid (HCl)

Regarding immersion in HCl solution, as show in Figure 3. The both type A and B mortars have much suffered high weight loss after 56 days immersion when compared with the same period of immersion in H_2SO_4 solution. Besides the weight loss increase between 56 to 180 days is not very significant as in case of immersion in H_2SO_4 solution. Mortars containing cement system with blast furnace slag (type B) suffered less weight loss at both 56 and 180 days and particularly at 180 days in comparison with mortars containing cement system with natural pozzolan (type A). Mortar A2 containing the same percentage of natural pozzolan (17.5%) and limestone (17.5%) shows the highest weight loss (11,66%) (See Figure 4) while mortar B2 containing the same percentage of blast furnace slag (17.5%) and limestone (17.5%) shows the lowest weight loss (4,01%). Detailed weight loss results are also presented in Tables 4 and 5.

Figure 4. Weight Loss (%) after 180 days of immersion in H_2SO_4 and HCl solutions



Source: Authors

The loss of weight of A and B specimens after immersion in HCl solution is opposite to the loss of weight of same specimens in H_2SO_4 solution; i.e. type A specimen's weight loss in H_2SO_4 solution is lowest while in HCl solution is highest and the opposite is verified with type B specimens.

As been described by other authors the rate of degradation in HCl solution is governed primarily by the diffusion of acid species through the degraded layer to the undamaged specimen. Depending on the pH of the acid zones different mineralogical composition form during degradation (Elkhadiri *et al*., 2002). As degradation proceeds, first portlandite dissolves transferring calcium ions to the pore solution. A solution-filled space is produced thus increasing porosity. At the same time porosity can be reduced by the precipitation of the corresponding calcium salt of the acid depending on its solubility (Thongsanitgarn *et al*., 2012). As well, once portlandite is depleted, the pH of the pore solution falls below about 12.4 and, along with the dissolution of AFm and AFt, decalcification of the calcium silicate hydrate phases (C-S-H) proceeds causing a substantial decrease in mechanical strength and a further increase in porosity (Makhloufi *et al*., 2012).

Weight loss in hydrochloric acid is mainly due to the release of calcium from portlandite into the solution. However, at acid pH values below 2 significant releases of aluminum and iron can also occur. As well during degradation by hydrochloric acid the acid ions penetrated the whole sample causing changes in both the crystalline and C-A-S-H phases transforming the hardened cement paste in the transition zone material. Chloride ions diffuse far beyond the degraded layer increasing the thickness of the transition zone where monosulphate is converted into Friedel's salt and ettringite. The microstructure and integrity of the degraded layer are important for the acid resistance of cement because they determine the ability of the layer to remain as a protective barrier on the surface during attack. Particularly, it has been found out that the replacement of Portland cement by supplementary cement materials rich in aluminum affects favorably the microstructure of the degraded layer (Itim *et al*., 2011).

In the current study it was verify that mortars type A (natural pozzolan + limestone) have suffered higher loss in hydrochloric acid. So although we assume that type A specimens contain the lowest amount of crystal CH (resulting in less reaction with sulphate ions) the rate of diffusion of acid species (HCl) through the degraded layer to the undamaged specimen is higher than in B type specimens (blast furnace slag + limestone). Thus, in type A specimens portlandite dissolved quicker than in type B transferring more calcium ions to the pore solution which caused higher loss of weight. On the other hand, in type B mortars (produced with limestone and blast furnace slag) we can assume that the rate of diffusion of ions penetrating the whole sample was slower thus causing less changes in both the crystalline CH and C-A-S-H phases and resulting in lower degradation by hydrochloric acid immersion.

Table 4. Type A specimen's test results after curing and being immersed in different aggressive solutions. Type A: 65% Clinker + 35% (natural pozzolan + limestone)

	Test	A1	A2	A3
Water Curing 28d	Strength (Mpa)	36.02	35.4	48,3
	Porosity by MIP (%)	13,96	13,67	13,35
Immersion in H_2SO_4 solution	Strength loss (%)	0,40	1,77	3,35
	Weight loss (%) 56 d	0,52	0,17	0,34
	Weight loss (%) 180 d	8,10	7,68	3,79
	Porosity increase (%)	8,66	8,55	9,35
Immersion in HCl solution	Strength loss (%)	47,86	38,40	38,12
	Weight loss (%) 56 d	8,49	9,19	6,94
	Weight loss (%) 180 d	10,75	11,66	9,90
	Porosity increase (%)	13,94	13,73	15,78

Source: Authors

Table 5. Type B Specimens test results after curing and being immersed in different aggressive solutions. Type B: 65%Clinker + 35% (blast furnace slag + limestone)

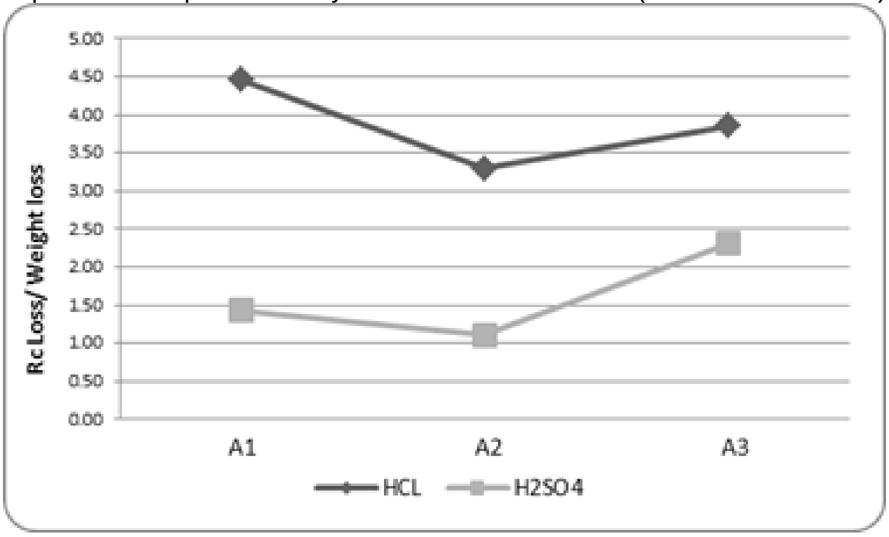
	Test	B1	B2	B3
Water Curing 28d	Strength (Mpa)	37,3	46.2	47.0
	Porosity by MIP (%)	12.73	12.40	11.47
Immersion in H_2SO_4 solution	Strength loss (%)	14,62	15,48	25,21
	Weight loss (%) 56 d	1,70	2,41	1,20
	Weight loss (%) 180 d	10,20	13,94	10,94
	Porosity increase (%)	6,78	7,54	13,58
Immersion in HCl solution	Strength loss (%)	16,41	15,80	25,66
	Weight loss (%) 56 d	5,50	4,01	3,28
	Weight loss (%) 180 d	6,19	4,01	5,70
	Porosity increase (%)	6,89	7,69	13,78

Source: Authors

3.5 RELATIONSHIP BETWEEN WEIGHT LOSS AND COMPRESSIVE STRENGTH LOSS

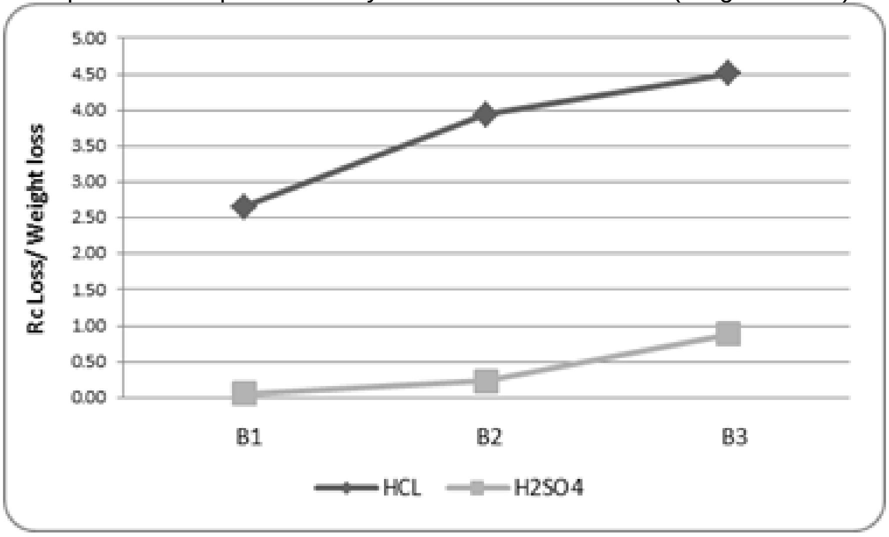
A significant correlation between weight loss and compressive strength loss was found after 56 days of exposure to sulphuric and hydrochloric acid solutions. This is in agreement with some authors (Turkel *et al*., 2007). The relationship between weight loss and the loss of compressive strength is shown in Figure 5.

Figure 5: Relationship between weight loss and compressive strength loss after 180 days exposure to sulphuric and hydrochloric acid solutions (Pouzzolan mixtures)



Source: Authors

Figure 6: Relationship between weight loss and compressive strength loss after 180 days exposure to sulphuric and hydrochloric acid solutions (Slag mixtures)



Source: Authors

It should be noted that there is a descending correlation between weight loss and loss of strength for type A mortar made of limestone and pozzolan. Contrarily there is ascending correlation for type B mortar containing limestone and slag. A discrepancy between weight loss and strength loss after exposure to acidic media was also reported in other studies (Chang *et al*., 2005; De Belie *et al*., 1996).

The correlation coefficients between weight loss and compressive strength loss are 0.77 for mortars type A and 0.70 for mortars type B immersed in HCl solution. For immersion of mortars type A and B in H_2SO_4 solutions, the such correlation coefficients are 0.99 and 0.81 respectively. The relationship between changes in weight and compressive strength change is not of same order of magnitude for both aggressive environments. For type A mortars after immersion in H_2SO_4 solution the loss of strength is less important with respect to weight loss. The opposite is observed for the immersion in HCl solution wherein the compressive strength change is higher than the loss of weight change. While in type B mortars the weight loss follows the strength loss trend in both environments for immersion in H_2SO_4 and HCl solutions.

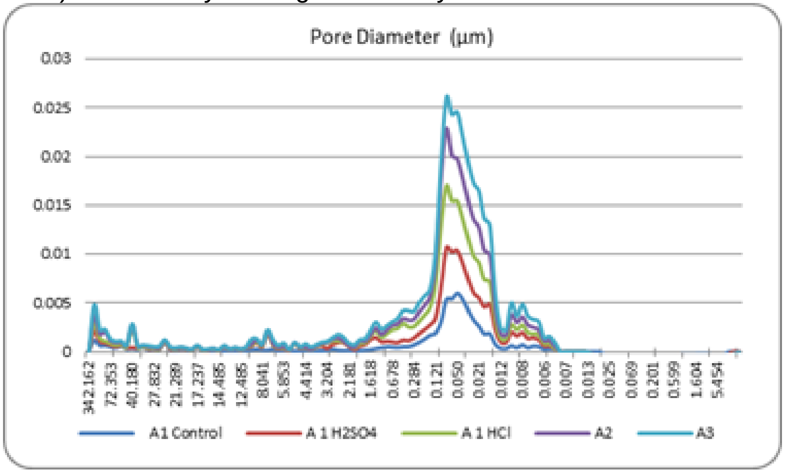
A similar correlation between weight loss and loss of compressive strength of limestone mortars with quaternary binders after 12 weeks' immersion in H_2SO_4 solutions has been reported in other studies (Makhloufi, *et al*., 2012). Accordingly, the weight loss reflects the successive deterioration of mortars specimens starting from the exposed surface and moving inwards. The fundamental factors controlling weight loss from the exposed surface are the calcium hydroxide content and the existence of a deteriorated or protective zone. Slag have a significant role in slowing down the kinetics of the acidic reaction by reducing the acid diffusion into the mortar matrix (Makhloufi, *et al*., 2012).

3.6 CHANGES IN POROSITY AFTER IMMERSION IN AGGRESSIVE SOLUTIONS

Pore size distribution before immersion and porosity increase after immersion in aggressive solutions was determined by MIP- mercury intrusion porosimetry. This technique provides a pore size distribution from the nanometer to micrometer range, as well as measures of total porosity and threshold diameter (Giesche *et al*., 2006).

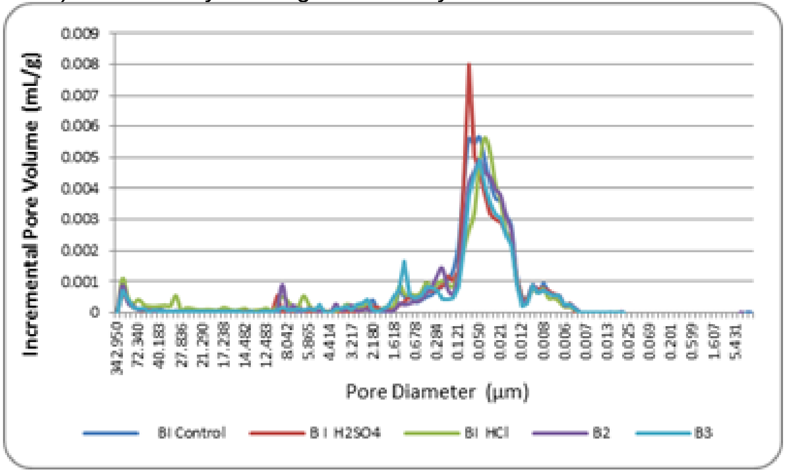
Figs. 7, and 8 present pore size distribution of different mortar types A and B after 28 days curing. Total porosity is presented in Tables 4 and 5, respectively.

Figure 7: Pore size distribution of Type A mortars – 65% Clinker + 35% (natural pozzolan limestone) after 28 days curing and 56 days of immersion in H_2SO_4 and HCl



Source: Authors

Figure 8: Pore size distribution of Type B mortars – 65% Clinker + 35% (blast furnace slag + limestone) after 28 days curing and 56 days of immersion in H_2SO_4 and HCl



Source: Authors

Mortar samples produce with natural pozzolan and limestone present a higher total porosity between 13.35 to 13.96% than type B mortars produced with blast furnace slag and limestone. In both mortar types most pores are below 2 µm. However, in mortar type A most pores are between 0,012 to 0,35 µm, while in mortar type B most porosity is between 0,012 to 0,15 µm pore size.

The effect of supplementary cement materials on the reduction of pore size distribution is also presented in (Panesar *et al.*, 2014). Different pore sizes are associated with varying amounts of CSH and a pore structure of the hydrated products more refined.

Figs. 7 and 8 compare the percentage increase in porosity given by MIP after 56 days of immersion in H_2SO_4 and HCl solutions. They give the pore size distribution changes in type A and B mortars for the same immersion period. The increase of porosity of type A mortars when immersed either in H_2SO_4 or HCl solution is in general higher than of B type mortars after being in the same conditions.

After immersion in HCl solution type A mortar shows the higher increase in porosity which is in agreement with loss of weight and loss of compressive strength results discussed in previous sections. MIP study confirms that mortar based on natural pozzolan and limestone have low resistance to HCl aggressive solutions. In turn, increase of porosity by MIP after immersion in HCL solution in relatively smaller for type B cement with blast furnace slag combined with limestone after immersion in HCL solution particularly in B1 and B2 mortars.

Regarding the increase of porosity by MIP after immersion in H_2SO_4 solution for 56 days both mortars types have suffered an increase of the same order of magnitude, between about 7 to 8% except B3 mortar where the increase of porosity was higher.

In Figure 8. It can be observed that porosity between 0,2 to 2 µm increased significantly after immersion of type A2 mortar for 56 days in HCl solution. While after immersion in H_2SO_4 for the same period the porosity has increased mainly between 0,06 to 0,12 µm pore sizes, where a peak is mainly detected in the pore size distribution graph.

Regarding the increase of porosity in type B2 mortars after immersion in HCl solution for the same period it appears to occur an increase in finer porosity, between 0,07 to 0,015 µm. Concerning the immersion in H_2SO_4 solution for the same period the porosity has also increased mainly between 0,06 to 0,12 µm pore sizes, where a similar peak is also detected.

4 CONCLUSIONS

Development of new binders using less clinker content as contribution to reduce CO_2 emissions and related Climate change was the main motivation of this research work.

The results showed that the addition of limestone filler, blast furnace slag, natural pozzolan, incorporated simultaneously in cement improves the mechanical behaviour of the binders. In addition, resistance to attacks of sulphuric acid

(H_2SO_4) and hydrochloric acid (HCl) solutions, depend on the proportion and the type of combination between mineral addition.

From the results obtained the following conclusions can be drawn:

The simultaneous incorporation of limestone filler, blast furnace slag and natural pozzolan plays a complementary role in the development of compressive strength of mortars based limestone.

Mortars containing blast furnace slag achieved highest compressive strength, the higher strength was found on B3 mortar (10% Limestone and 25% Blast furnace slag). In opposition, the lowest compressive strength was found on A1 mortar (25% Limestone and 10% natural pozzolan).

Natural pozzolan (type A) based-mortars suffered less weight loss during immersion in H_2SO_4 solution in comparison with the ones produced with blast furnace slag (type B). This might be a consequence of a better developed pozzolanic reaction. Mortar A3 containing 25% natural pozzolan and 10% lime stone showed the higher resistance in H_2SO_4 solution ; B3 mortar specimens containing the highest percentage of blast furnace slag show the highest decrease in strength (about 25.7 %) after immersion in H_2SO_4 solution.

Mortars type A (natural pozzolan + limestone) have suffered higher weight loss in hydrochloric acid (HCl) solution immersion. The rate of diffusion of acid species (HCl) through the degraded layer to the undamaged specimen is higher than in B type specimens .A1 mortar specimens containing 10% of natural pozzolan and 25% of limestone presented the highest decreased is compressive strength, of about 47.9 after immersion in HCl solution.

MIP study confirms that mortar based on natural pozzolan and limestone have low resistance to HCl aggressive solutions.

Regarding the increase of porosity by MIP after immersion in H_2SO_4 solution for 56 days both mortars types A and B have suffered an increase of the same order of magnitude.

The integration of the ternary combination of limestone and blast furnace slag as limestone and natural pozzolan has gained considerable importance because of the requirements of environmental safety, for the strength gain and more durable construction in the future.

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