CIMENTURI HIBRIDE ALCALINE.
PARTEA a III-a – DURABILITATE ŞI APLICAŢII INDUSTRIALE▲
HYBRID ALKALINE CEMENTS.
PART III. DURABILITY AND INDUSTRIAL APPLICATIONS

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This part of the research explored the reaction of hybrid alkaline cements when they are exposed to acid (0.1-N HCl), sulphates and seawater. The hybrid cement used in the experiments comprised essentially metallurgical slag generated by the Fe and Zn industries. A standard Portland cement was used as the reference system. The findings showed that performance of these hybrid cements was similar to the results observed for the control. In a subsequent industrial trial, the concrete made with this experimental binder was successfully used in the manufacture of precast blocks and pavers.

Lucrarea prezintă rezultatele cercetărilor privind comportarea cimenturilor alcaline hibride în soluţii agressive acide (HCl 0,1N), cu sulfaţi şi apă de mare. Cimenturile hibride utilizate în cadrul experimentărilor conţin zguri rezultate din metalurgia Fe şi Zn. Cimentul portland standard este folosit ca sistem de referinţă. Rezultatele au arătat că aceste cimenturi hibride au avut performanţe asemănătoare cu cele observate pentru cimentul de referinţă. Într-un studiu ulterior, efectuat la nivel industrial, s-a constatat că betonul realizat cu acest liant hibrid a fost folosit cu succes la fabricarea de blocuri prefabricate şi pavele.

Keywords: *hybrid cement, alkali activation, geopolymer concrete, durability, blocks*

1. Introduction

For many years, supplementary cementitious materials (SCMs) such as slag, natural pozzolans and fly ash have been used to reduce the Portland clinker content in cement, as attested to by numerous examples described in the literature [1-5]. This practice has, moreover, been acknowledged by legislation the world over as a way of generating different types of cement. Unanimous reports on the significant improvements observed in cementitious systems, coupled with the obvious contribution to sustainability, have consolidated usage. Substantial increases in SCM content, however, often induce a perceptible decline in early mechanical strength. The scientific community is studying the development of *hybrid cements* as a solution to this problem.

Hybrid cements are characterised by a low Portland clinker or cement content (under 30 %) and high proportions of aluminosilicate materials, primarily industrial by-products (such as blast furnace slag, phosphorous slag, Ni or Zn production plants or type F fly ash [6-7]).

These cements need to be alkali activated to develop technologically viable early mechanical strength. The alkaline activators used may be liquid (NaOH, sodium silicate or potassium silicate solutions, etc.) or solid (Sodium or potassium silicates, carbonates, sulphates etc.). The concentration and amount of activator used in each case depends largely on the CaO content in the cement blend and specific SCMs reactivity.

Another important characteristic of these hybrid cements is that their hydration gives rise to a mix of reaction products, normally C-A-S-H and (N,C)-A-S-H gels. Studies are presently underway to determine the compatibility of these products. Thus far, the results of thermodynamic trials on synthetic gels indicate that they interact and tend to evolve toward a single material [8-10].

Another important feature of these hybrid cements is their durability. Most of the papers on cement durability published to date address Portland or alkali-activated slag or fly ash cements. Consequently, little is known about hybrid cement durability. The present study focuses on the behaviour of hybrid cement when exposed to attack by aggressive chemical solutions (0.1-N HCl, sodium sulphates and seawater). The hybrid binder studied here consisted of a blend of 12 % Portland clinker + 88 % [blast furnace (BFS) + zinc slag +alkali activator]. The results showed that "normal" concretes for manufacturing precast construction

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elements (blocks and pavers) can be made with this cement.

2. Experimental

High durability Portland cement (CEM HS) was used as a control in this study, while the experimental material was a hybrid cement (CEM HY) obtained by blending 12 % Portland clinker with two types of slag (BFS + Zn slag) and alkali activator. **Table 1** gives the chemical composition of the materials used, as determined with a PHILIPS PW 2400 X-ray fluorescence spectrometer fitted with a PW 2540 VTC sample changer. These findings showed that the main components of the slag were CaO, SiO_2 and Al_2O_3, although the oxides prevailed over the CaO in the Zn slag.

The XRD trace for the BFS exhibited a characteristic halo between 20 and 25º, denoting the high vitreous phase content of this component. The sole diffraction line observed may have been generated by small amounts of akermanite (C_2MS_2). The Zn slag contained a higher percentage of crystalline phases, such as quartz, anorthite ($CaAl_2Si_2O_8$), franklinite (Zn, FE and Mn oxide), iron chromate and $Zn_2(SiO_4)$. Both the clinker and the CEM HS, in turn, exhibited the characteristic alite, belite, C_3A and C_4AF phases.

Three-centimetre cubic specimens were prepared with both binders (CEM HS and CEM HY) in a 24-specimen steel mould. The (95 % quartz, CEN EN 196-1) sand/binder ratio was 3:1 and the water/cement ratio was 0.45 for both mortars. All the materials were cured for 20 hours in a chamber at 24±1 ºC and 99 % relative humidity, subsequently removed from the moulds and returned to the chamber for a further 28 days.

Four 28-day specimens per test age were submerged in each aggressive solution. The ratio between the volume of aggressive solution to the specimen area tested was 10, further to ANSI/ANS [11-12] recommendations on leaching methods, and the solution was refreshed after 1, 2, 3, 7, 28, 56 and 90 days. Specimens were tested after 7, 28, 56 and 90 days. The specimens were removed from the solution at the test age, air dried on filter paper and then for 24 hours (to a constant weight) in a kiln at 40 ºC. The dry cubes were compression tested to failure on an IBERTEST (Autotest – 200/10-SW) testing frame. The aggressive media used were: **S**= sodium sulfate solution (4.4 % Na_2SO_4); **M**= seawater (ASTM D 1141-90); **Cl** = 0.1-N HCl solution (pH = 1.5).

Three-cm cubic paste specimens were also prepared with the HS and HY cements using a water/cement ratio of 0.32 and cured under the same conditions for subsequent mineralogical (BRUKER D8 Advance diffractometer) and microstructural (JEOL JSM 5400 scanning electron microscope) characterisation.

3. Durability against aggressive media

3.1 Mechanical strength

Figure 1 shows the variations in mortar compressive strength (in %) versus immersion time. In both mortars, strength was generally observed to rise with time in 4.4 % Na_2SO_4 and seawater, although CEM HS behaved somewhat erratically when submerged in seawater.

In acid media, however, strength declined substantially in both cements. While the decline was initially steeper in the hybrid cement, in the 90-day materials the effect was more intense in the HS control. In any event, these findings

Table 1

XRF chemical analysis
Compoziția chimică determinată prin metoda FRX

Oxide (%)	CEM HS	Clínker	BFS[1]	ZnS[2]
SiO_2	32.85	22.41	37.42	37.17
Al_2O_3	6.86	5.59	11.47	16.50
Fe_2O_3	5.44	3.84	0.66	11.40
MnO	0.05	0.03	0.19	0.87
MgO	2.39	3.24	10.62	3.71
CaO	46.60	60.42	32.71	17.79
Na_2O	0.66	0.78	1.47	0.44
SO_3	2.00	1.46	2.96	1.14
K_2O	0.63	1.20	1.19	1.49
TiO_2	0.27	0.20	0.50	0.79
P_2O_5	0.1	0.23	0.05	0.13
P.C.	2.15	0.60	0.76	8.27
Total	100	100	100	100

[1]BFS = granulated blast furnace slag
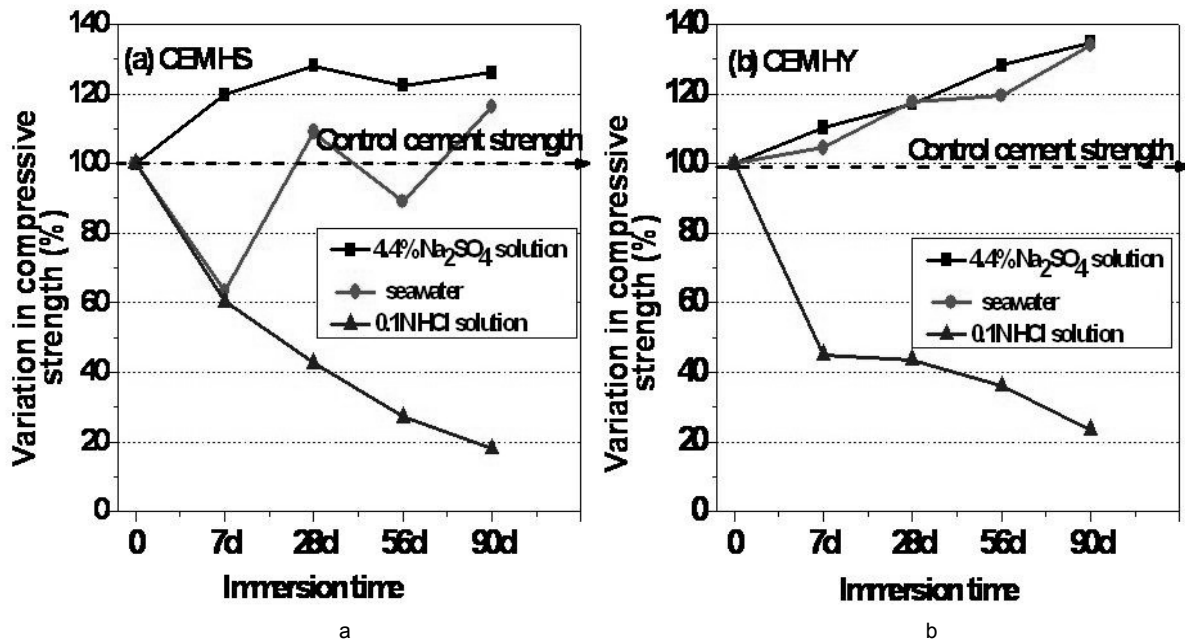[2]ZnS = Waelz process Zn slag

a

b

Fig. 1- Mortar compressive strength (%) vs time (days) submerged in aggressive solutions: / *Evoluţia rezistenţei la compresiune a mortarului (%), funcţie de timp (zile), a probelor imersate în soluţii agressive* (a) CEM HS (control); (b) CEM HY (hybrid cement).
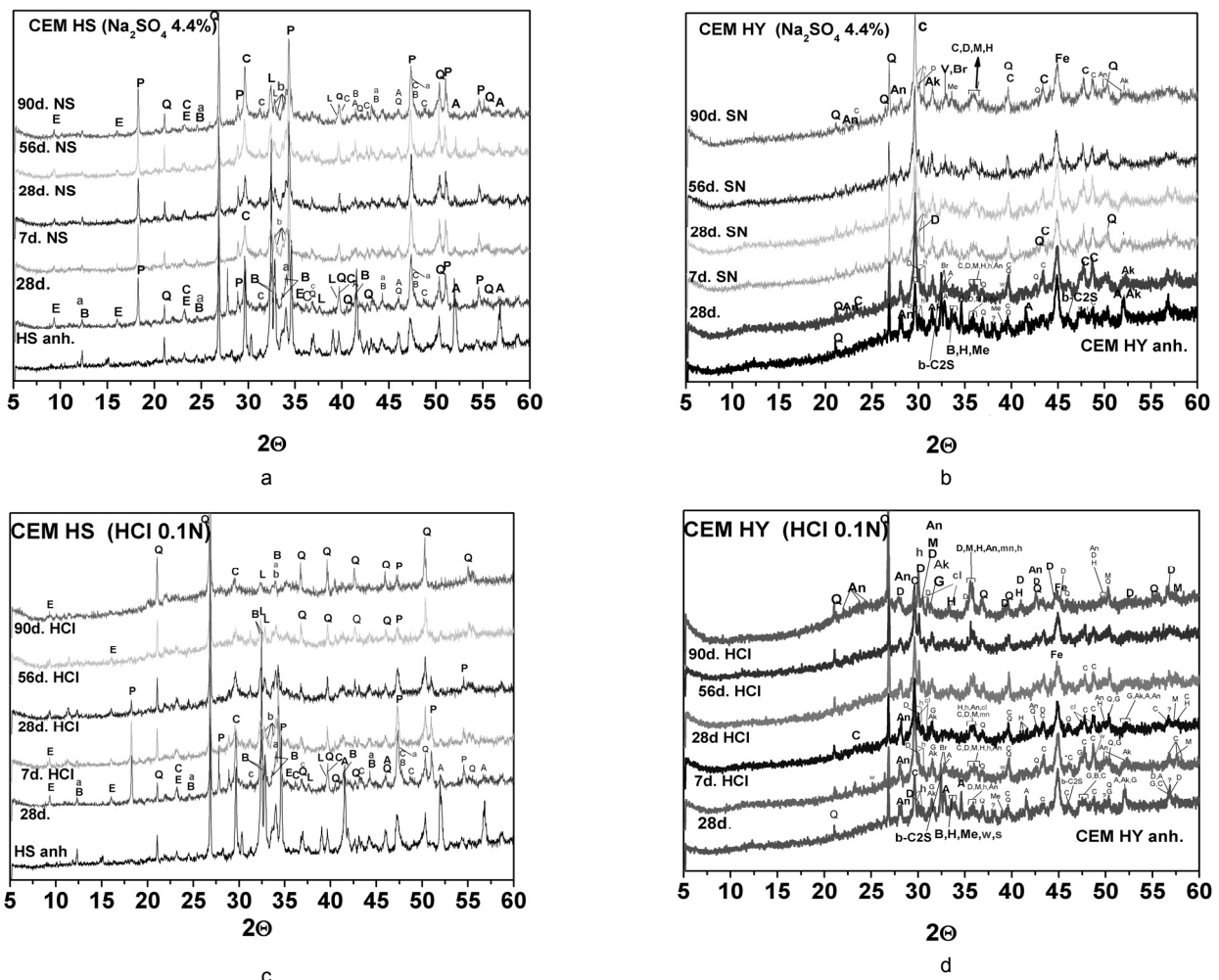

a

b

c

d

Fig. 2 - Diffractograms for HS and HY cement pastes submerged in aggressive media for different durations / *Difractogramele pastelor întărite de ciment HS şi HY, imersate în soluţii agressive, pe durate diferite:* (a) CEM HS in sodium sulfate; (b) CEM HY in sodium sulfate; (c) CEM HS in HCl and (d) CEM HY in HCl *Legend:* anhydrous materials: A= C_3S; B= brownmillerite (C_4AF); L= larnite Ca_2SiO_4; Q= quartz; An= anorthite; Ak= akermanite; D= diopside; G= gehlenite; h= hedenbergite; H= hematite; le= leucite; M =maghemite; new phases: C= calcite; E= ettringite; P= portlandite; cl= calcium silicate chloride; w= willemite.

showed that when hybrid cements are exposed to aggressive media, their behaviour is wholly comparable to the performance of conventional Portland cements. No differential pattern seemed to be present.

The materials were characterised with XRD and scanning electron microscopy (SEM/EDX) to determine whether, as a result of exposure to the aggressive media, any new reaction products formed or the products initially formed had decayed.

Figure 2 reproduces the XRD patterns for the two cements after immersion in sodium sulfate and acid media during six exposure times (in light of their similarity to the results for the sodium sulfate solution, the seawater findings are not shown). When the control cement, HS, was exposed to sulfates, ettringite was observed to form from the outset, although its content did not increase significantly with exposure time. Ettringite formation was not identified in the hybrid cement, HY, at any age, although the presence of low crystallinity, non- XRD-detectable ettringite could not be ruled out.

On the diffractogram for cement HS exposed to acid, the signals associated with portlandite ($Ca(OH)_2$) tended to disappear over immersion time (see Figure 2(c)). During acid attack, the accelerated calcium hydroxide leaching induced by the proton reduces aqueous phase alkalinity, raises paste porosity and may hasten decay. When the proton concentration is sufficiently high, it may even attack the C-S-H gel [13-14].

No portlandite appeared in CEM HY, either because none formed or because it formed in insufficient quantities to be detected by XRD. A proton attack against the gel or gels forming in these cements cannot be ruled out, however. As proven in other studies [8-9], the (C-A-S-H and (N,C)-A-S-H) gels in these hybrid cements take up substantial amounts of tetrahedral aluminium in their structure, in addition to having a lower Ca/Si ratio than the C-S-H gels generated during conventional portland cement hydration. The presence of tetrahedral aluminium together with sodium ions (that balance the charge) in these gels raises their acidity and with it their stability in acid media. Under very severe attack, however, de-alumination may in fact occur, as reported for alkali-activated slag and fly ash mortars exposed to acid attack [13-17].

Figure 3 reproduces micrographs and the respective microanalyses for the cements submerged for 28 days in sodium sulfate. Two types of ettringite were clearly observed in cement HS. The first, primary ettringite, was the reaction product formed by the interaction between the gypsum and aluminates in the cement in the initial stages of hydration. This ettringite had a characteristic needle-like morphology (Figure 3, point 1). The second type, secondary ettringite, whose incipient crystals appeared in tiny clusters, formed as a result of sulfate attack (Figure 3, point 2).
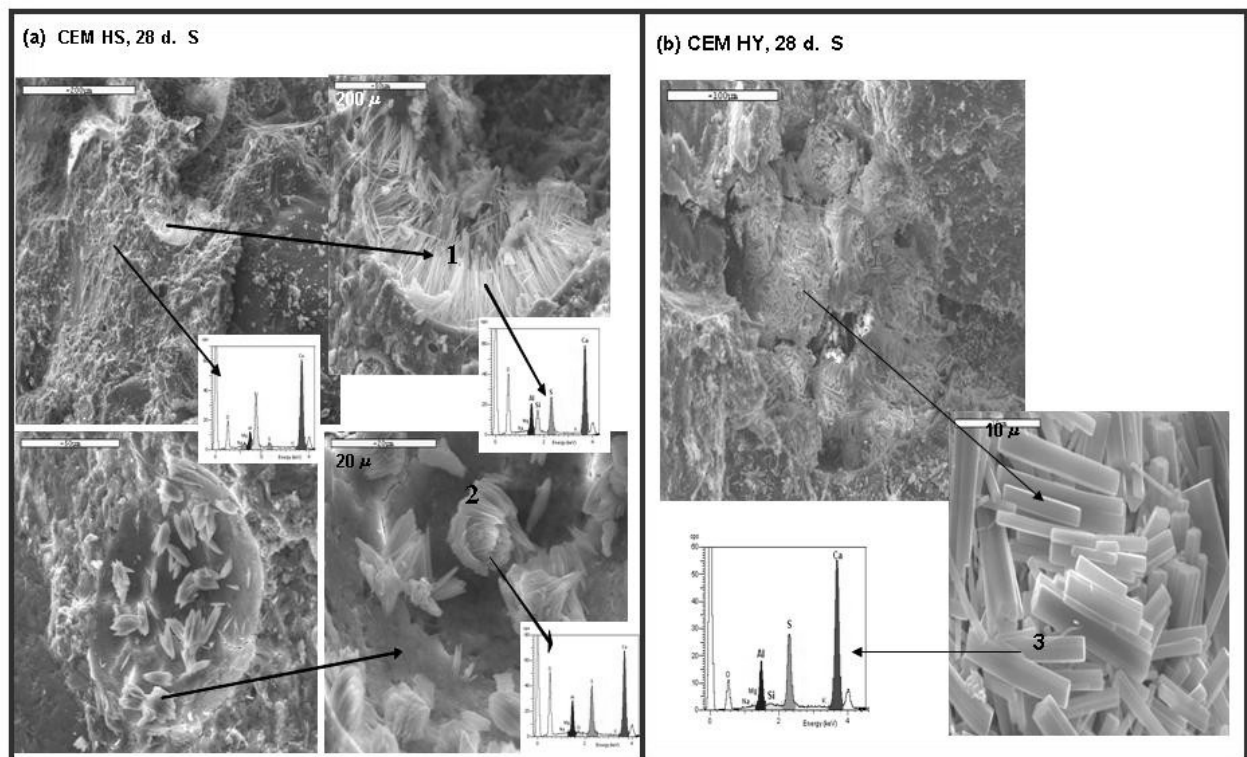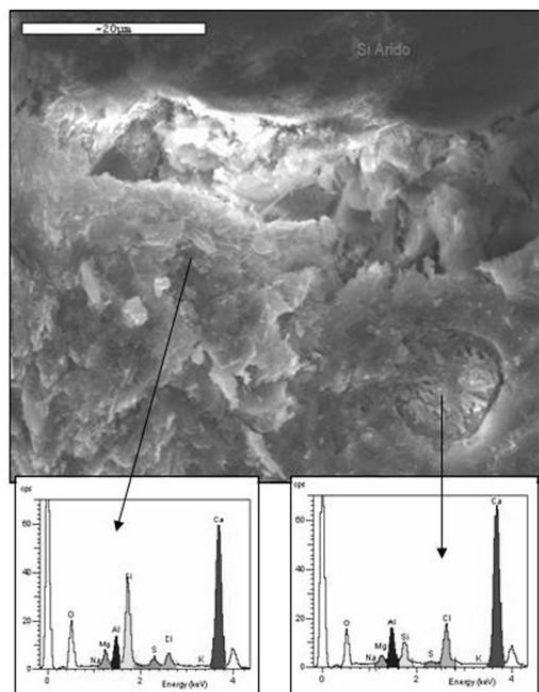

Fig. 3 - SEM micrographs and respective microanalyses for (a) HS and (b) HY submerged for 28 days in a sodium sulfate solution/ *Micrografiile SEM și microanalizele elementale respective, pentru (a) HS și (b) HY, imersate în soluție de sulfat de sodiu timp de 28 zile :* 1 = primary ettringite; 2 = secondary ettringite; 3 = microcrystalline ettringite.
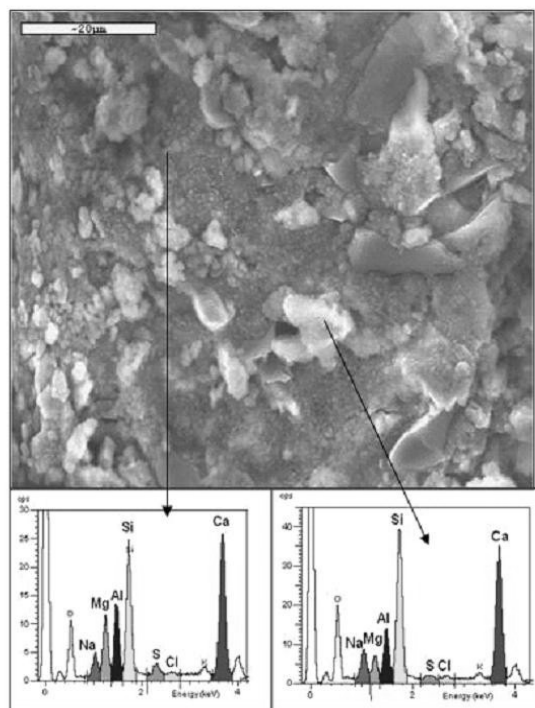
Fig. 4 **-** Micrographs and EDX/SEM analyses for (a) CEM HS and (b) CEM HY submerged in 0.1-N HCl for 28 days / *Micrografiile SEM şi microanalizele elementale EDX, pentru (a) CEM HS şi (b) CEM HY, imersate în soluţie de HCl 0,1N timp de 28 zile.*
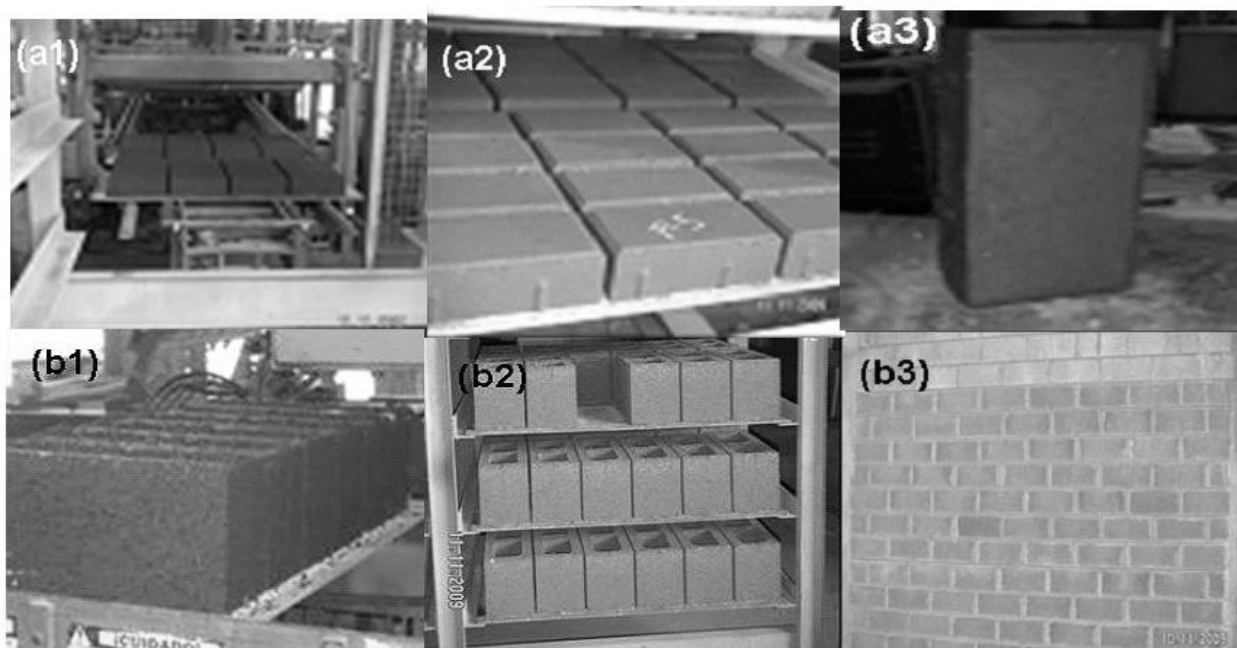

Fig. 5 - Production of (a) type 14 wall blocks (≈ 10 % CEM HY); (b) type 6 pavers (30 % CEM HY) / *Producerea industrială de (a) blocuri de zidărie (≈ 10 % CEM HY); (b) pavele (30 % CEM HY).*

Small ettringite crystals were also detected sporadically in cement HY. Since that cement contained no sulfates in its initial composition, the ettringite in question could only have been the result of the attack by the sulfates present in the aggressive solution. These ettringite crystals were very small, however, and their quantity insufficient to be detected by XRD. They may have formed in and filled pores, which would explain the slight increase in mechanical

strength observed in Figure 1.

The micrographs in Figure 4 depict the CEM HS and CEM HY after 28 days of exposure to the 0.1-N HCl solution. Chloride ions were detected in the HS cement matrix, together with greater porosity as a result of the acid attack. The fact that no Cl⁻ ions were identified in cement HY did not preclude the presence of small amounts of Cl⁻ ions disseminated in the inner matrix. The

microanalyses of this matrix clearly showed that the gel forming in these hybrid cements contained aluminium, sodium and even magnesium, in addition to calcium and silica. In other words, this gel had a lower Ca/Si ratio than the HS material.

When is exposed to aggressive media (sulfate, seawater and acid attack) hybrid cement exhibits behaviour very similar to the performance observed in conventional Portland cements. Of the three aggressive media tested in this study, the 0.1-N HCl solution reacted most aggressively with both cements.

4. Industrial Application

Finally, a series of industrial trials were conducted in which concretes for precasting pavers and blocks were manufactured with cement HY. The binder/aggregate ratio used for these two products differed. In the blocks the cement dosage was around 10 %, whereas in the pavers, where higher mechanical strength was required, the dosage was on the order of 30 %. Figure 5 depicts the elements precast with these hybrid cement concretes. Both the 2- and 28-day materials met mechanical strength requirements. The only difference worthy of mention between these elements and the products made with Portland cement was their slightly lower density.

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