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# EFFECT OF LIMESTONE FILLER ON THE SULFATE RESISTANCE OF LOW $C_3A$ PORTLAND CEMENT

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## ABSTRACT

This paper presents an investigation of the sulfate resistance of fillerized cements. Test was carried out on mortars containing one type II cement and two type V Portland cements with different $C_3S$ contents. Limestone filler was used as 0%, 10%, and 20% of replacement by cement weight. The test method is based on the ASTM C 1012 procedure. Expansion, flexural and compressive strengths, solution consumption, and x-ray diffraction analysis were determined at different exposure times up to 1 year. After 360 days of sulfate immersion, the results indicate that the 10% of limestone filler replacement shows no significant effect on sulfate performance of these cements, whereas 20% of limestone filler (LF) causes detrimental effects on sulfate durability. This behavior can be explained by the changes in the hydration degree, capillary porosity, and type of hydration products produced by LF addition. Gypsum and ettringite were only detected in mortars exposed to sulfate solution. *© 1998 Elsevier Science Ltd*

## Introduction

Since 1980, the use of limestone filler (LF) in cement manufacture has increased in several countries due to economical and ecological considerations. Several standards in the world report the addition of LF up to 35% by cement weight in composite cements (1). Filler addition increases the hydration rate of Portland cement, especially of $C_3S$, during the early ages (2–4), leading to achievement of the same strength level with a higher water-to-cement ratio.

Sulfate attack is related to gypsum and expansive ettringite formation. These compounds are the products of the reaction between sulfate ions with calcium hydroxide (CH) and $C_3A$ hydrates, respectively. In terms of cement composition, $C_3A$ is the main compound involving sulfate resistance of cement. However, CH released from silicates hydration affects the sulfate resistance of low $C_3A$ Portland cements (5).

Little bibliographic information about the sulfate performance of Portland cement with LF addition, especially for low $C_3A$ cements, is available (6–8). Hooton (8) concluded that

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TABLE 1
Chemical composition and physical properties of Portland cements used.

| | Type V low $C_3S$ ($PCV_{low}$) | Type V high $C_3S$ ($PCV_{high}$) | Type II (PCII) |
|---|---|---|---|
| Oxide composition (% by weight) | | | |
| $SiO_2$ | 23.66 | 21.00 | 22.19 |
| $Al_2O_3$ | 3.00 | 3.29 | 4.08 |
| $Fe_2O_3$ | 5.41 | 4.68 | 3.16 |
| CaO | 62.14 | 66.00 | 62.74 |
| MgO | 0.60 | 0.67 | 0.58 |
| $SO_3$ | 1.59 | 2.20 | 2.48 |
| Alkalis | 0.72 | 0.82 | -,- |
| Loss by ignition | 1.61 | 1.23 | 1.86 |
| Calculated composition (% by weight) | | | |
| $C_3S$ | 40 | 74 | 51 |
| $C_2S$ | 38 | 4 | 26 |
| $C_3A$ | 0 | 1 | 6 |
| $C_4AF$ | 15 | 14 | 10 |
| Fineness Blaine ($m^2$/kg) | 313 | 306 | 285 |
| Compressive strength (MPa) (ASTM C 349) | | | |
| 3 days | 11.4 | 27.3 | 23.3 |
| 7 days | 17.6 | 29.2 | 35.8 |
| 28 days | 32.7 | 32.5 | 42.8 |
| Expansion (%) (ASTM C 452) | | | |
| 14 days | 0.015 | 0.012 | 0.023 |
| 90 days | 0.025 | 0.021 | 0.048 |
| 360 days | 0.030 | 0.045 | 0.162 |

carbonate additions have no influence on sulfate resistance, except for $C_3A$ dilution, when large filler replacements (up to 5%) are used in type I Portland cement. Some authors also suggested that LF can improve the performance of high $C_3A$ Portland cement due to calcium carboaluminate formation (9). For low $C_3A$ cements, both conveniences do not exist; thus, the replacement of cement by LF could have detrimental effects on sulfate resistance.

This paper reports 1-year results related to the effect of LF addition on the sulfate resistance of low $C_3A$ Portland cements. A comprehensive review of LF effects on the paste structure and their relation to degradation of mortar exposed to sodium sulfate solution are presented.

## Materials and Procedures

An ASTM type II cement (PCII) and two type V cements with very different $C_3S$ contents ($PCV_{low}$ and $PCV_{high}$) were used in this investigation. The physical and chemical characteristics of the Portland cements are detailed in Table 1. For all cements, the ASTM C 452 expansion at 14 days was lower than the limit for sulfate-resistant Portland cement (0.04%).

Filler cements were made using a 10% and 20% (by weight) replacement of Portland by LF. A good LF containing 85% of $CaCO_3$ and a Blaine fineness of 710 kg/$m^2$ was used.

For each Portland and filler cement, a series of mortar specimens (285 × 25 × 25 mm) was cast according to ASTM C 1012 (sand-to-binder material ratio of 2.75 and water-to-binder ratio of 0.485). Mortar specimens were stored in a moist cabinet for 24 h, then removed from the mold and cured in saturated limewater solution until they achieved 30 ± 3 MPa compressive strength. In this test method, the expansion limit for sulfate-resistant cement is 0.1% at 1 year (10).

After curing, each series of prisms was individually immersed in a plastic tank containing a 5% sodium sulfate solution (0.35M $Na_2SO_4$). The pH of the test solution was readjusted periodically by titration with a combined solution (0.35M $Na_2SO_4$ + 2N $H_2SO_4$) using a few drops of phenolphthalein as pH indicator. The consumption of titration solution was measured and the ratio of mortar-bar volume to sulfate-solution volume was maintained at 1:4 throughout the test.

At 0, 28, 56, 90, 180, and 360 days of sulfate immersion, the specimens were tested to determine the expansion and strength of mortar. Flexural strength tests were carried out on mortar bars using centerpoint loading and a span length to deep ratio of 2.5. At each test age, two bars were tested and five values of strength were obtained for each bar. Compressive strength tests were conducted on four pieces of prisms using a compression machine adapted for testing this small cube (25 mm). The relative flexural and compressive strengths after a given time of exposure were calculated as the ratio of strength in solution and the strength in water. Expansion was measured on the remaining prismatic specimens.

Fragments of the broken prisms were powdered to determine the mineralogical composition by x-ray diffraction (XRD). XRD analyses were performed on a diffractometer (Phillips X'Pert) using Cu-Kα radiation, equipped with a graphite monochromator, operating at 40 kV and 20 mA.

## Results

### Sulfate Demand

Figure 1 shows the cumulative titration solution added during 360 days for each mortar. It can be observed from these curves that the consumption rate progressively decreased at all exposure times. At early ages, the stronger demand of sulfate is related to the solubility of the calcium hydroxide from specimen surfaces (11). Later it is related to the attack progress. For $PCV_{low}$ mortar, the sulfate demand is null after 90 days of immersion, whereas mortars with LF have a high sulfate demand and the consumption rate shows a growing trend until 180 and 360 days for 10% and 20% of LF, respectively. Sulfate demand of $PCV_{high}$ mortars is greater than that of $PCV_{low}$ owing to the extended CH solubility process. In $PCV_{high}$ LF mortars, sulfate demand increases, revealing a greater mortar–solution interaction at all ages. For PCII mortars, sulfate demand values have a raising rate during all times, and there is more sulfate demand in mortars with 10% and 20% of LF than plain mortar.

Generally, it was noted that increasing filler replacement increases the total volume of sulfate solution added. At the end of the test, solution demand shows a clear dependence on $C_3S$ and filler contents in cement (12).

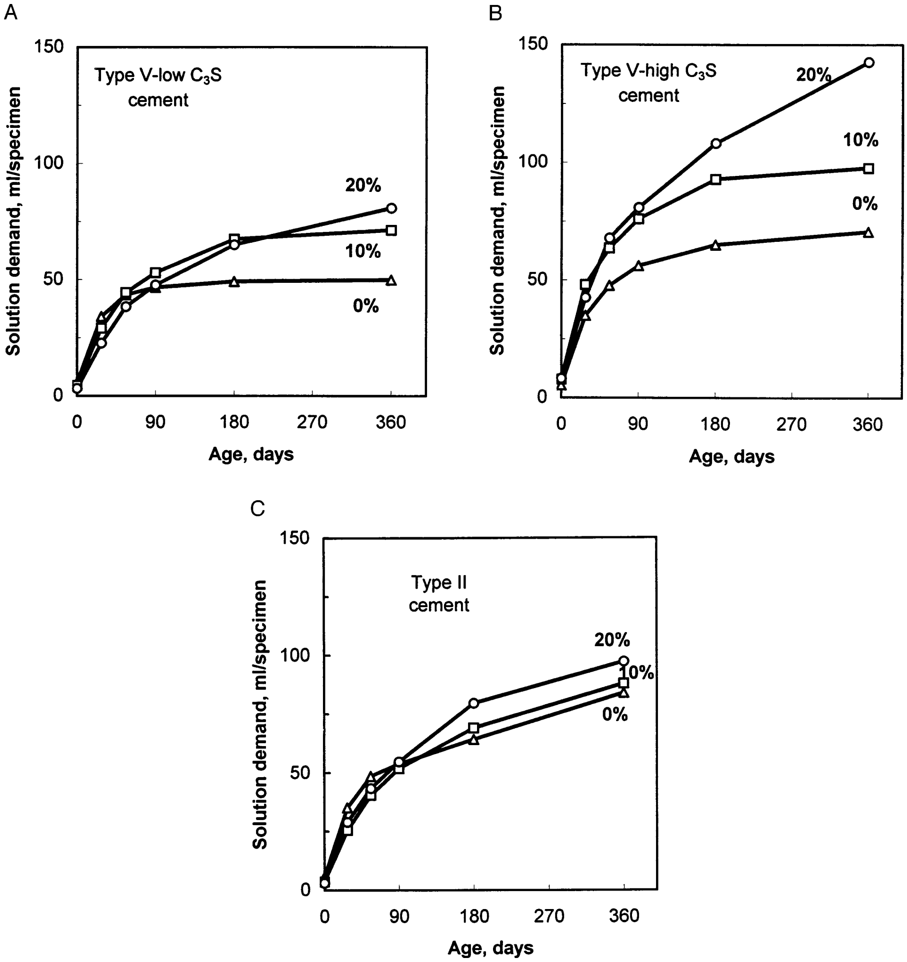

FIG. 1.
(*A*–*C*) Cumulative sulfate solution consumed during 360 days of exposure.

## Expansion

The data on expansion of mortar prisms in sulfate solution for a period up to 360 days for all cements are shown in Figure 2. These data indicate that PCV$_{\text{low}}$ mortar has the lowest expansion during the test, whereas PCV$_{\text{high}}$ mortar has a high expansion, similar to that of PCII mortar instead of the low $C_3A$ content in PCV$_{\text{high}}$ cement.

For PCV$_{\text{low}}$ cement, mortars containing LF have a high expansion compared to plain mortar. However, expansion of PCV$_{\text{low}}$ + 10% LF mortar (0.066% after 360 days of exposure) was lower than the failure limit proposed by Patzias (10) for sulfate-resisting cements (0.100% at 1 year).

PCV$_{\text{high}}$ mortars with 0% and 10% LF have a similar expansion evolution until 180 days of exposure, then PCV$_{\text{high}}$ + 10% LF mortar had a small enlargement. For 20% of LF

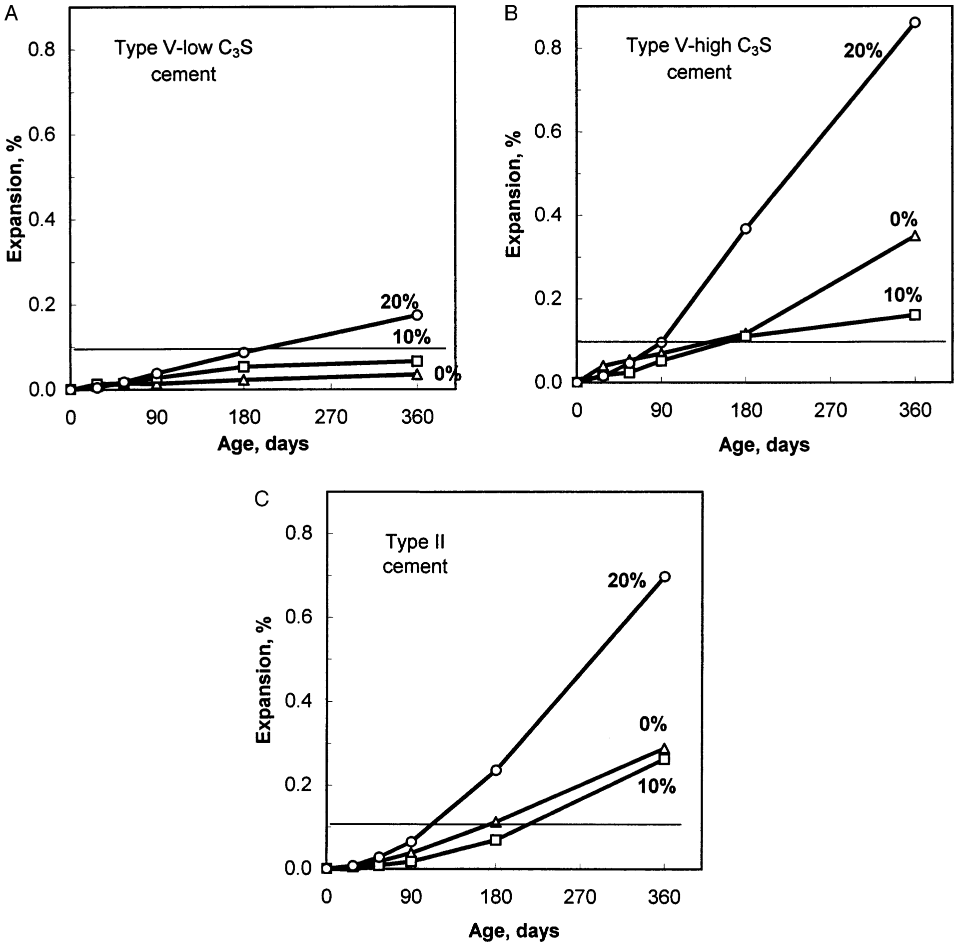

FIG. 2.
(*A–C*) Expansion in mortars during 360 days of exposure.

replacement, the expansion was higher than that of the plain mortar, attaining a double expansion value at 1 year. All $PCV_{high}$-based cements are not sulfate-resistant cements according to the failure expansion criteria.

For PCII mortars, the expansion of specimens containing 10% of LF was observed to be lower than that of the plain cement at all test ages, whereas the expansion of specimens containing 20% LF had a very large expansion.

## Flexural Strength

Figure 3 shows the development of relative flexural strength with time of sulfate exposure. Flexural strength exhibits a typical behavior in a sulfate environment. The first time, flexural strength increased more in sulfate solution than in water curing due to the pores being filled,

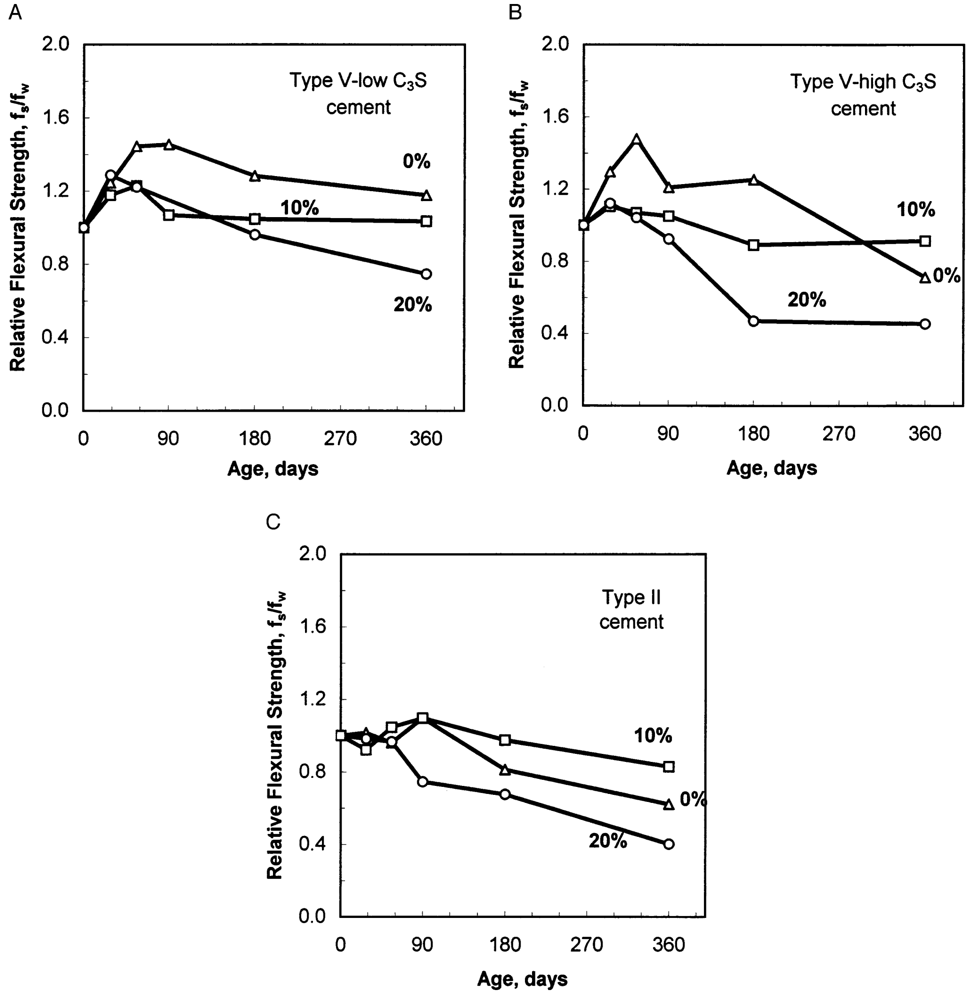

FIG. 3.
(*A–C*) Flexural strength in sulfate solution related to flexural strength in water at the same age.

and then strength was retained or decreased due to the microcracking produced by expansive compounds of attack.

For $PCV_{low}$ and $PCV_{low}$ + 10% LF mortars, a high relative flexural strength ($f_{sulfate}$:$f_{water}$ $>1$) was obtained at all test times, whereas $PCV_{low}$ + 20% LF mortar showed a progressive decrease of strength after 90 days of sulfate immersion. All $PCV_{high}$ mortars had strength loss in sulfate at the end of the test. Flexural strength reduction appeared earlier when LF content increased (180, 90, and 56 days for 0%, 10%, and 20% LF, respectively).

In PCII-based mortars, the relative flexural strength declined after 90 days for 0% and 10% replacement levels. It had a remarkable retrogression after 28 days for PCII + 20% LF mortar.

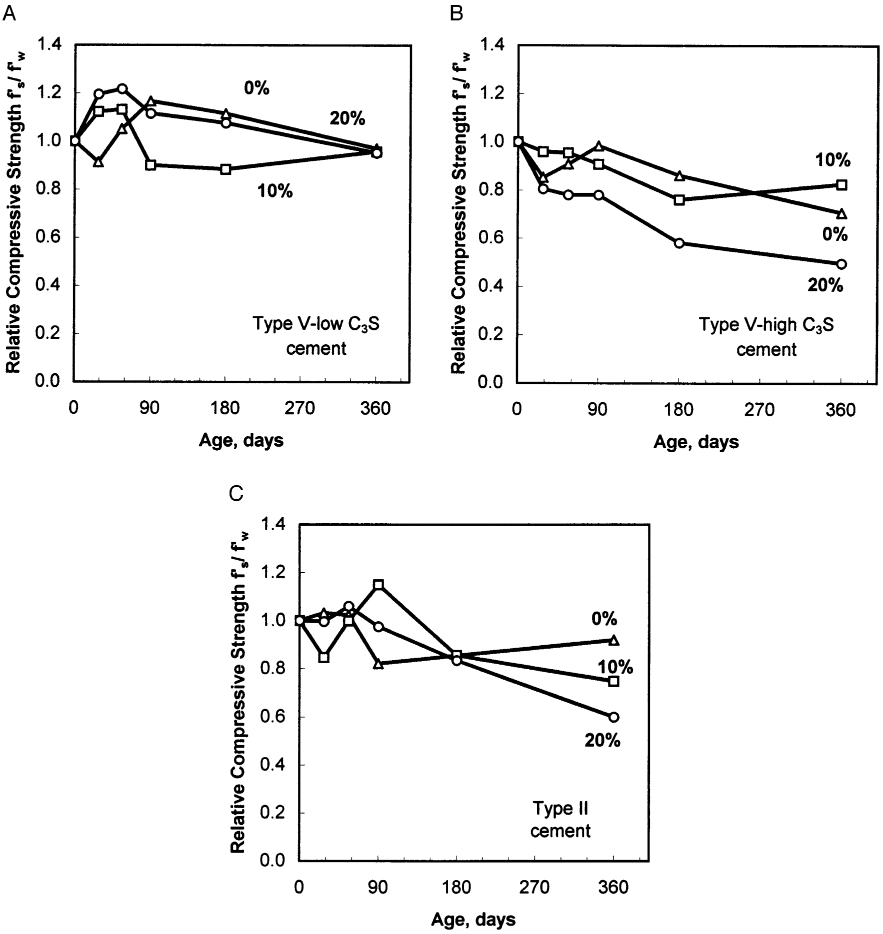

FIG. 4.

(*A*–*C*) Compressive strength in sulfate solution related to compressive strength in water at the same age.

## Compressive Strength

Figure 4 shows the relative compressive strength reduction data in mortar specimens exposed to sodium sulfate solution. For $PCV_{low}$ mortars, these curves show a strength gain at early exposure times and then slight decreases in strength evolution of mortars containing 10% and 20% of LF. After 360 days of exposure, the strength reduction was approximately 5%.

The strength reduction curves were markedly different for $PCV_{high}$ + LF mortars. For 10% of LF added, the compressive strength had a slight reduction during all test ages ($<$10%). However, the strength reduction in $PCV_{high}$ + 20% LF from test beginning was considerable, and the strength reduction reached 50% by the end of the test.

PCII mortars with 0% and 10% of LF showed some erratic behavior, but they retained more than 80% of compressive strength at 1 year. PCII + 20% LF showed a rapid strength decline after 28 days in solution, and the strength reduction was significant (~40%).

## XRD Analysis

XRD patterns at 360 days of sulfate exposure are shown in Figure 5. $PCV_{low}$ mortar diffractogram showed only peaks characteristic of gypsum ($2\theta = 11.70°$) as product of sulfate attack. Mortars containing $PCV_{low}$ + LF cement exhibited some ettringite peaks ($2\theta = 9.08°$, $15.78°$) in addition to a well-defined gypsum peak. There was no evidence of the presence of thaumasite peaks ($2\theta = 9.24°$, $16.07°$) in mortars with LF. In $PCV_{high}$ plain mortars, gypsum peaks appeared to be accompanied by ettringite peaks. In both type V cements, ettringite formation was the result of the reaction between sulfate ions and the ferroaluminate hydrates (5). Both $PCV_{high}$ + LF mortars exhibited ettringite and gypsum peaks, whereas thaumasite is absent. The intensity of the gypsum peak was very strong in mortar with 20% of LF.

PCII plain mortars showed the two typical products of the sulfate attack: gypsum and ettringitte. The gypsum peak was highest in the plain mortar, whereas the mortar containing 20% of LF had a strong ettringite peak.

## Discussion

The effects of LF addition on the diverse parameters used to evaluate the sulfate resistance of cements are summarized in Table 2.

For plain mortars, $PCV_{low}$ is the only sulfate-resistant cement, whereas $PCV_{high}$ and PCII are not sulfate-resistant cements. The poor sulfate resistance of type V Portland cement with high $C_3S$ content ($PCV_{high}$) has been amply discussed by the authors in a previous paper (5).

For the three cements used, the most favorable behavior was obtained with the 10% of limestone replacement leading to a similar or better performance than those of plain cements. On the other hand, the sulfate performance of cements with 20% of LF was the worst. These mortars have a short time to reach the expansion limit, the greatest reduction in flexural and compressive strengths at test end, and the highest solution demand. When cement contains high $C_3S$ or moderate $C_3A$, the deterioration rates increase due to the extended interaction between sulfate ions and the unstable hydrates in the mortar. This trend was similar in all cements used despite their quite different compositions, which can be explained by the results of mineralogical analysis by XRD presented previously.

From the XRD pattern of $PCV_{low}$ mortar, the absence of ettringite and a slight peak of gypsum can be seen clearly after 1 year of sulfate immersion. This cement is highly sulfate resistant due to the low $C_3A$ and low $C_3S$ contents. In both $PCV_{low}$ + LF cements, gypsum formation originated by acidic sulfate attack was detected with a strong intensity when the amount of filler replacement increased. A low intensity of ettringite peaks also was detected, but mortars have a very low expansion. Sulfate demand observed was very low due to the small extent of CH leaching from paste to solution. It had a null rate because attack is dominated by gypsum deposition into the mortar without enlargement of exposed surface by cracking.

For $PCV_{high}$ mortar, the presence of gypsum was found at early ages (90 days) of sulfate immersion, leading to the ettringite formation coming from the ferroaluminate phase at later ages. Expansion-cracking deterioration appears as a manifestation of this formation. Gypsum deposi-

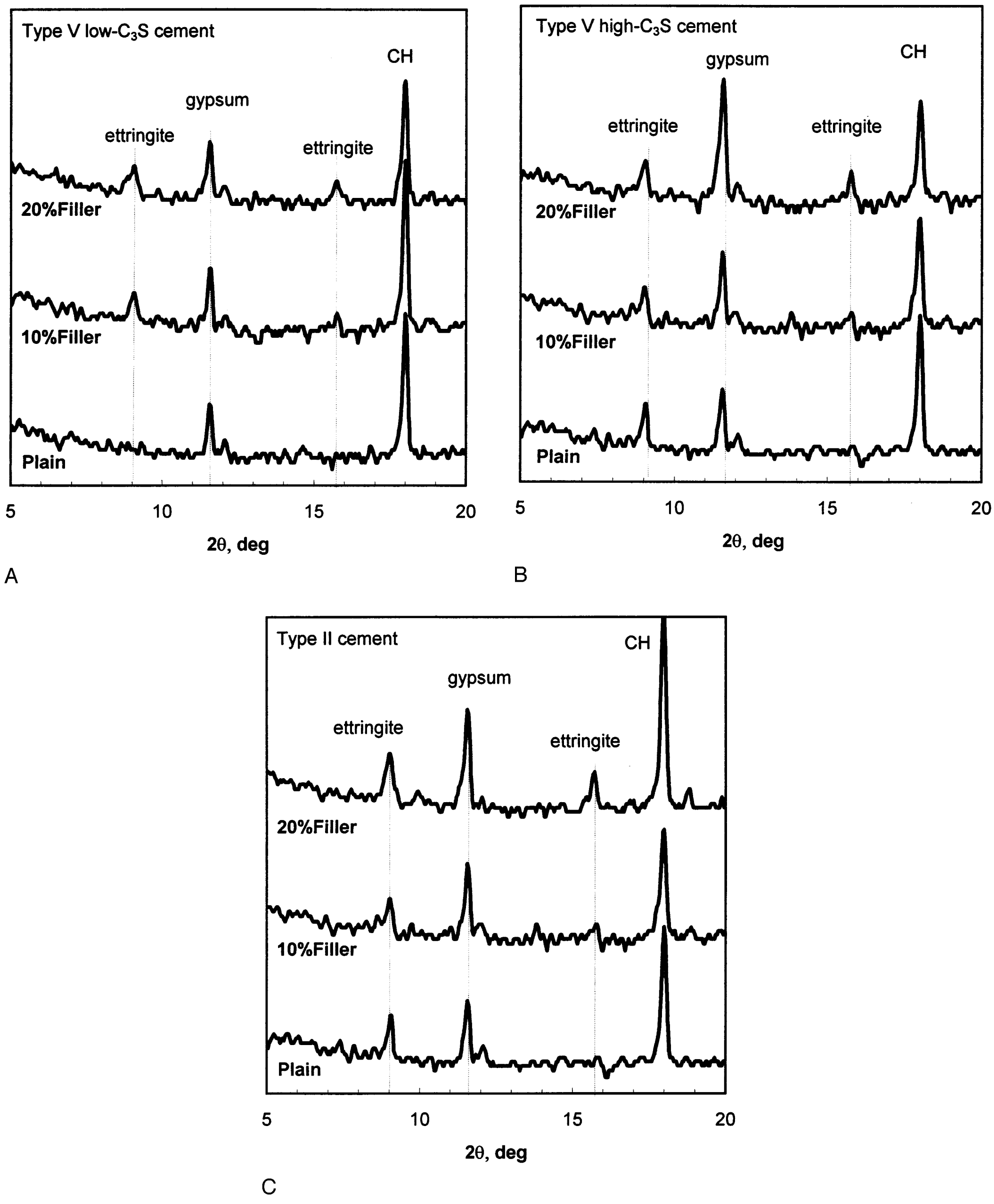

FIG. 5.
(*A*–*C*) XRD patterns of mortars after 360 days of sulfate exposure.

tion at the aggregate–paste interface causes expansion, and the cracking of mortar leads to a larger surface exposed (5,13). Then, gypsum dominates the paste environment and the ettringite is expansive. For cement with LF, the same degradation mechanism occurs vigorously in $PCV_{high}$ + 20% LF and is attenuated in $PCV_{high}$ + 10% LF. Expansion, flexural strength loss, and a upward trend of sulfate demand are evidence of this type of attack.

TABLE 2
Time to failure expansion (0.1%), flexural strength reduction, and compressive strength reduction for mortars exposed to sulfate solution for 360 days.

| | Type V low $C_3S$ | | | Type V high $C_3S$ | | | Type II | | |
|---|---|---|---|---|---|---|---|---|---|
| Limestone filler (%) | 0 | 10 | 20 | 0 | 10 | 20 | 0 | 10 | 20 |
| Time to 0.1% expansion (days) | 1260 | 857 | 208 | 148 | 164 | 92 | 165 | 209 | 108 |
| Reduction of flexural strength at 360 days (%) | −18 | −3 | 25 | 29 | 9 | 55 | 38 | 17 | 60 |
| Reduction of compressive strength at 360 days (%) | 3 | 4 | 5 | 29 | 17 | 50 | 8 | 25 | 40 |

For the PCII cements, XRD analyses show that ettringite crystal grows at early ages of sulfate immersion and then the peak of gypsum appears. This sequence is typical in mortars containing monosulfoaluminate prior to sulfate immersion. PCII + LF mortars show the same sequence of attack product formation appearing at early ages in mortar containing 20% of LF.

This observation on LF cement performance can be explained qualitatively by the effects of LF on the composition and structure of hydrated paste and its relation with sulfate performance. LF addition may have various effects in mortars as follows: an increase of the hydration rate of Portland cement grains, a dilution effect of cement components, the reaction between LF and $C_3A$ to form carboaluminates, and the deleterious thaumasite formation at later ages in some sulfate environments.

It has been proved that the presence of filler grains leads to an increase of hydration rate of cement grains, especially the $C_3S$ hydration when the filler is limestone (2–4). For the type II cement used in this experimental work, Bonavetti (14), using nonevaporable water determination, found that the degree of hydration increased from 0.60 to 0.74 at 7 days when 10% or 20% of limestone was added. However, the hydration degree was the same after 28 days of water curing. This increment of hydration rate implies a greater amount of CH liberated in the mortar and a decrease of porosity at the same age when the filler is added. In mortar, the amount of CH is controlled by the initial water-to-cement ratio and the local environment. This environment is influenced significantly by the LF grains, which act as nucleation sites for the reaction products (CH and C-S-H), and then the $C_3S$-hydration reaction proceeds rapidly.

In sulfate resistance of mortar, the amount of CH and the location of the crystals play a decisive role (15). Precipitation of CH crystals at very early ages causes massive deposits of oriented crystals on the paste–aggregate interface, which lead to an inevitable increase of porosity in this region. Thereafter in a sulfate environment massive gypsum formation around the aggregates has been observed by several authors (5,13,16). According to Mehta (17), the presence of CH to form a gypsum environment also is needed for the expansive ettringite formation. In this case, LF increases the Portland cement hydration rate, leading to the precipitation of CH located around the filler grains and the aggregate surfaces. CH crystal is a weak point in sulfate attack, and at later ages it will not be removed, as occurs when pozzolanic additions are used.

Another negative aspect of sulfate resistance due to the increase of hydration rate is the poor strength development of LF cements after 28 curing days, which does not permit the long-term improvement of mortar microstructure. In a previous paper (18), the potential capacity of mortar to generate new bonds after the sulfate exposition was introduced as a significant factor to reach at deferred time of mortar cracking.

It is important to point out that the water-to-cement ratio also increases when fillers are used as replacement for Portland cement. Capillary porosity depends on the water-to-cement ratio and hydration degree; depending on these values the porosity can increase or decrease. At the same level of strength, porosity can be the same in Portland cement and filler cements as demonstrated by Ranc et al. (19). But, cements with LF have a poor porosity reduction in the long term, because the hydration rate increases at an early age, consuming the reactive cement grains, and the LF does not contribute, at later ages, as pozzolanic admixtures by the pore size refinement process. At the hydration degree of 0.8, the calculated capillary porosity of paste is 19.7%, 24.5%, and 29.4% for 0%, 10%, and 20% of LF content. This increase in porosity implies a large space in mortar for calcium hydroxide formation, which reacts with sulfate ions to form gypsum, leading to a predominant gypsum environment needed for expansive ettringite. The initial capillary porosity is an important factor in the induction phase of the attack, but in a sulfate environment the porosity is modified by the proper attack and the hydration process.

The dilution effect of the reactive compound in Portland cement in a sulfate environment ($C_3A$ and $C_3S$) by addition of mineral admixtures has been indicated as a contributor to improvement of the sulfate performance of high $C_3A$ Portland cements (7,8). To examine a dilution effect produced by the addition of mineral admixtures, some authors (20,21) replaced cement with finely ground quartz, which can be assumed to be a filler addition that increases the hydration rate (2,22). They concluded that the dilution effect could improve the sulfate resistance of high or moderate $C_3A$ cement, but this effect appeared to be insufficient to obtain a sulfate-resistant cement.

In this work, $C_3A$ dilution has no significance because all cements used had a low $C_3A$ content. On the other hand, the dilution of $C_3S$ can be analyzed in association with the increase in $C_3S$ hydration rate produced by addition of LF.

During cement hydration, carbonate ions coming from LF compete with the sulfate ions from gypsum to react with aluminate ions from $C_3A$, leading to modification of hydration products. Reaction products from the $C_3A$ phase of Portland cement in the presence of LF are monocarboaluminate, monosulfoaluminate, and ettringite. Tricarboaluminate was not found by several researchers (4,14,23). Vernet and Noworyta (9) reported that the stability of monocarboaluminate is better than that of the monosulfoaluminate and aluminate hydrates, and they inferred a relative greater resistance of LF cements exposed to sulfate attack. For PCII pastes, monocarboaluminate formation was detected by XRD after 3 days of water curing. Monosulfoaluminate transformation to monocarboaluminate and ettringite was detected at 28 days (14), which is in agreement with above reference (9). But, XRD results of mortars with LF immersed in sulfate solution provided evidence of ettringite formation. Vernet et al.'s suggestion overlooks that ettringite is more stable than monocarboaluminate in a sulfate environment, as reported in a solubility product and stability study (24).

In a sulfate environment, thaumasite formation ($CaSiO_3$“$CaSO_4$“$CaCO_3$“$15H_2O$) has been proposed as a deterioration mechanism of concrete or mortar containing carbonate aggregates (25). Recently, studies carried out by the Building Research Establishment (26) suggested this type of sulfate attack in limestone-filled cement mortars. According to Berra and Baronio

(27), thaumasite formation occurs when there is an external supply of sulfates and carbonates ions in the presence of active alumina at higher relative humidity and reduced temperature (about 5°C). In this type of attack, the main mechanism of deterioration is the breakdown of the calcium-silicate-hydrate phases in the hardened cement paste (25). Gaze (28) reported that thaumasite was only found when the paste contained ettringite originating at early stages of sulfate attack and a high gypsum content.

In this experimental work, the mortar bars were stored at laboratory temperature (~21°C) for 1 year. Consequently, one basis environment condition for thaumasite formation is not present and only ettringite formation would be expected. Second, a gypsum environment is found only for $PCV_{high}$ at later ages, which provided the conditions for expansive ettringite formation derived from the ferroaluminate phase (5). In PCII mortars, the ettringite peak appears before that of gypsum, due to the ettringite formation derived from the $C_3A$ hydrates phase, but thaumasite was not found. XRD patterns provided evidence that the principal deleterious compounds of sulfate attack were gypsum and ettringite for all cements containing LF.

In the authors' opinion, LF addition had little influence on the mineralogical nature of sulfate attack products for low $C_3A$ cements. Mortars with longer expansion and higher flexural strength loss have the strongest ettringite peak in XRD patterns, corroborating that it is responsible for expansion-cracking deterioration in a sulfate environment.

Finally, the combination of these effects produced by filler addition may increase or decrease the sulfate performance of LF cements depending on the mineralogical composition of the Portland clinker, the amount of filler replacement, and the equilibrium between the increase of hydration degree before the exposure and the water-cement increase by filler addition. Thus, addition of LF to low $C_3S$ cement can produce a blended cement with sulfate performance similar to that of plain cement when the amount of filler added does not increase inadequately the capillary porosity or this will be compensated for by the increase of hydration degree at early ages. When porosity enlarges due to the filler addition, the interaction between mortar and solution increases, leading to a vulnerable blended cement.

Results from this work shows that LF has no detrimental effects on sulfate resistance for 10% replacement, whereas it accelerates the deterioration rate for all cements with 20% of LF. To extend this conclusion, the effect of different combinations and proportions will need to be investigated by a long-term test.

## Conclusions

The results of this laboratory test showed that the replacement of low $C_3A$ Portland cements with LF can significantly affect the sulfate resistance of composed cement.

A 10% replacement of LF caused no significant changes in the sulfate performance of cements. This replacement proportion was favorable in cement containing unstable compounds in a sulfate environment.

Sulfate performance of mortars containing 20% of LF was worsened in all cases. Detrimental effects were more relevant when high $C_3S$ or moderate $C_3A$ contents were in the Portland cement.

The addition of LF may increase or decrease the sulfate performance of blended cements depending on the mineralogical composition of the Portland clinker, the amount of filler replacement, and the equilibrium between the increase of hydration degree before the exposure and the water-cement increases by filler addition.

Sulfate attack on Portland cements containing LF occurs without noticeable changes in the mineralogical nature of sulfate attack products. The main attack products are gypsum and ettringite.

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