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Effect of lignosulfonate, calcium chloride and their mixture on the hydration of RHA-blended portland cement

N.B. Singh*, V.D. Singh, Sarita Rai, Shivani Chaturvedi

Department of Chemistry, DDU Gorakhpur University, Gorakhpur, India

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Abstract

Hydration of 10 wt.% rice husk ash (RHA)-blended Portland cement has been studied in the presence of 2 wt.% $CaCl_2$, 1 wt.% lignosulfonate (LS) and a mixture of the two admixtures by using different methods. Free lime determinations and differential thermal analysis have shown that $CaCl_2$ accelerates the pozzolanic reaction of $Ca(OH)_2$ and RHA. In the presence of mixture of two admixtures, lower amount of water is required for consistency of the paste. IR spectral studies have supported that the mixture of the two admixtures act as a strong accelerator for cement hydration. The compressive strength is highest in the presence of a mixture of the two admixtures at 28 days of hydration. The admixtures did not prevent the deterioration of the blended cement in corrosive atmosphere. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Lignosulfonate; Calcium chloride; Hydration; Blended cement; Compressive strength

1. Introduction

The use of a variety of waste materials as supplementary cementing materials is growing. Blast furnace slag, fly ash, silica fume, rice husk ash (RHA), etc., have already been established as mineral admixtures for blended cement production [1–4]. As a supplementary cementing material, many unique properties of RHA have been reported by several investigators [5–15]. With fresh concrete mixtures pozzolanic additions, such as RHA, have the ability to reduce bleeding and segregation, and thus cause significant improvement in workability [5].

Except RHA, no other pozzolanic additions including silica fume has the ability to contribute to the strength of portland cement concrete at the early ages of 1 and 3 days [5]. The RHA-blended portland cement greatly improves the durability characteristics. RHA helped substantially to reduce the mass loss of concretes exposed to hydrochloric acid solution and largely reduced the expansion due to sulfate attack and alkali–silica reaction [15].

Effect of different admixtures on the hydration of portland cement is well documented; however, they are less studied on the hydration of blended cements especially the RHA-blended cement. $CaCl_2$ is a well-known accelerator [16] and lignosulfonate (LS) is a retarder [16] in portland cement hydration. These admixtures also modify the hydration process of RHA-blended cement.

In the present paper, the effects of 2% $CaCl_2$, 1% LS, and a mixture of both the admixtures on the hydration of RHA-blended ordinary Portland cement (OPC) have been studied and the results discussed.

2. Experimental

2.1. Materials

OPC was procured from Associated Cement, Thane, India. The oxide composition of OPC was determined with the help of X-ray fluorescence spectrometer at the Institut für Gesteinshüttenkunde, Technische, Hochschule, Aachen, Germany. The mineralogical composition of OPC was calculated with the help of the Bogue equation. These values are given in Table 1. The particle size distribution of OPC was measured with the CILAS laser particle size analyzer. The specific surface area was 325 m^2/kg.

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* Corresponding author. Tel.: +91-551-200-009; fax: +91-551-340-459.
E-mail address: dr_n_bsingh@rediffmail.com (N.B. Singh).

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Table 1
Oxide composition of Portland cement and RHA and mineralogical composition of Portland cement

Oxide/mineral phase	Composition (wt.%) Portland cement	RHA
SiO_2	19.75	65.2
Al_2O_3	4.84	
Fe_2O_3	3.26	0.2
CaO	62.66	0.2
MgO	4.19	0.9
K_2O	0.54	1.0
Na_2O	0.06	0.8
TiO_2	0.44	
PbO	0.07	
ZnO	0.09	
MnO	0.15	
P_2O_5	0.03	
SO_3	2.13	
C_3S	76.8	
C_2S	5.51	
C_3A	7.31	
C_4AF	9.92	

The rice husk was collected from a rice mill at Kasia, Kushinagar. First, it was burnt in open atmosphere and then ignited in a furnace at 650 °C for 1 h and stored in a polyethylene bag. The oxide of RHA composition is given in Table 1.

$CaCl_2$ and LS were used as admixtures. The admixture concentration was calculated with reference to the weight of binder.

2.2. Methods

2.2.1. Preparation of blended cements

Blended cements were prepared by replacing 5, 10, 15, 20, 25, and 30 wt.% of OPC by RHA. For this purpose requisite amounts of OPC and RHA were taken in a polyethylene bottle and thoroughly mixed for 1 h for each blend.

2.2.2. Determination of consistency

Consistency was determined with the help of 'Vicat apparatus.' The consistency of 10% RHA-blended OPC was determined in the presence of 2% $CaCl_2$, 1% LS, and in a mixture of 2% $CaCl_2$ and 1% LS. For this purpose solutions of appropriate concentrations of the admixtures were prepared and then added to the blended cement.

2.2.3. Determination of setting time

It was measured with the help of Vicat apparatus. The setting times of 10% RHA-blended OPC were measured in the presence of 2% $CaCl_2$, 1% LS, and a mixture of both admixtures.

2.2.4. Determination of compressive strength

Pastes of 10% RHA-blended portland cement were made with the addition of 2% $CaCl_2$, 1% LS, and a mixture of the two at a water–binder ratio appropriate for consistency measurement.

Three molds of each sample cement paste of the dimension 2 × 2 × 2 in. [3] were cast and after demolding moist curing was done for 7 and 28 days. Compressive strengths after 2 days were measured with the help of compression testing machine (AIM 304). Compressive strength reported is an average of three measurements.

2.2.5. Preparation of hydrated samples

Ten grams of blended cements were taken in polyethylene bags to which 5 ml of water or admixture solutions were added to get water/binder = 0.5. The mixture was thoroughly mixed by pressing between the fingers, then air was removed and sealed. The sealed bags were kept for different times and the hydration was stopped by adding isopropanol and ether to the mixture. The samples were dried at 105 °C, kept in polyethylene bags, which were sealed and stored in a desiccator.

2.2.6. Analysis of hydrated samples

Free lime in hydrated samples was determined by modified Franke extraction method [17].

Ca^{++} and OH^- ions were analyzed by titration.

The samples after particular hydration periods were analyzed using infrared spectroscopy, X-ray diffraction analysis, thermogravimetric analysis, and scanning electron microscopy.

2.2.7. Effect of corrosive atmosphere

Rectangular bars of 10% RHA-blended cement, 10% RHA-blended cement with the addition of 2% $CaCl_2$, and with the addition of a mixture of 2% $CaCl_2$ and 1% LS were prepared. The bars were kept under water for 28 days and then taken out and lengths measured. Now the bars were immersed into N/60 H_2SO_4 and expansions were measured at particular times.

3. Results and discussions

Consistency of OPC paste blended with RHA increased with increase in the amount of RHA. This is attributed to the higher specific surface area of RHA (>20 m^2/g) compared to portland cement (~ 8 m^2/g). The dose of RHA was optimized by measuring the initial and final setting times (Fig. 1). The initial and final setting times were found to be maximum at 10 wt.% of RHA, hence it was considered to be an optimum limit of RHA concentration. Effect of different admixtures was studied on 10 wt.% RHA-blended OPC.

Effect of 1% LS (a superplasticizer), 2% $CaCl_2$ (an accelerator), and a mixture of 1% LS and 2% $CaCl_2$ on the setting times of 10% RHA-blended OPC were measured and are given in Fig. 2. From the figure, it is clear that both the initial and final setting times were enhanced considerably in the presence of 1% LS indicating that it prolongs the

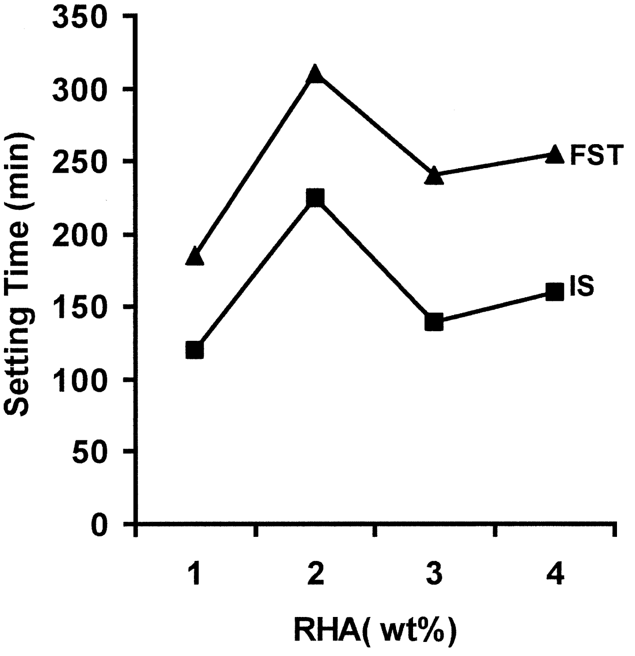

Fig. 1. Effect of RHA on setting time.

setting behavior. It shows that 1% LS acts as a retarder. The 2% $CaCl_2$, on the other hand, reduces both initial and final setting times showing that it acts as an accelerator in the hydration of RHA-blended OPC. However, in the presence of a mixture of 1% LS and 2% $CaCl_2$, the setting time values are higher than that in the presence of 2% $CaCl_2$ and lower than that in the presence of 1% LS.

The effect of admixtures on the consistency of 10% RHA-blended OPC is given in Table 2. From the table, it is clear that in the presence of 1% LS, the water/binder ratio is reduced considerably as is generally expected in the presence of a superplasticizer. In the presence of 2% $CaCl_2$ (an accelerator), the water/binder ratio is lower than that of control but higher than that in the presence of 1% LS. However, in the presence of a mixture of 1% LS and 2% $CaCl_2$, the water/binder ratio is the lowest. This indicates that water reduction is enhanced in the presence of a mixture of a superplasticizer (1% LS) and an accelerator (2% $CaCl_2$).

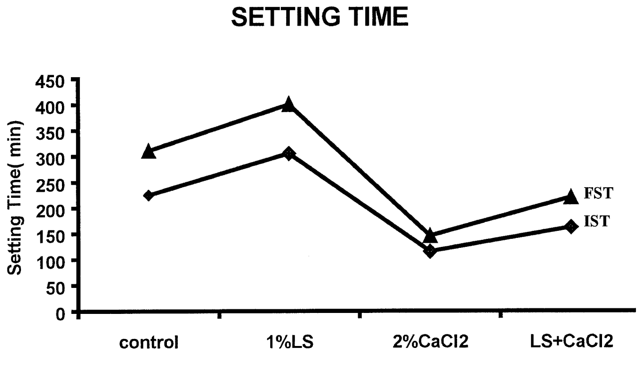

Fig. 2. Effect of admixtures on the setting time of blended cement containing 10% RHA.

Table 2
Variation of water consistency with admixtures

Composition	Water/binder
90% OPC + 10% RHA	0.42
90% OPC + 10% RHA + 2% $CaCl_2$	0.40
90% OPC + 10% RHA + 1% LS	0.38
90% OPC + 10% RHA + 2% $CaCl_2$ + 1% LS	0.37

The variation of free lime with hydration time is shown in Fig. 3. In the case of OPC, the free lime increases continuously with hydration time indicating that the hydration proceeds with time, whereas, in the presence of 10% RHA, it increased up to 7 days and then decreased up to 28 days of hydration, indicating that the detectable pozzolanic reaction of RHA starts only after 7 days. The 2% $CaCl_2$ accelerates the pozzolanic reaction and the amount of free lime liberated is much lower in its presence. In the presence of 1% LS, the pozzolanic reaction is retarded, whereas in the presence of a mixture of the two (1% LS and 2% $CaCl_2$) the extent of pozzolanic reaction lies in between that of 1% LS and 2% $CaCl_2$. The overall results on free lime measurements show that calcium chloride is a very good admixture for accelerating the pozzolanic reaction between RHA and calcium hydroxide obtained from the hydration of OPC.

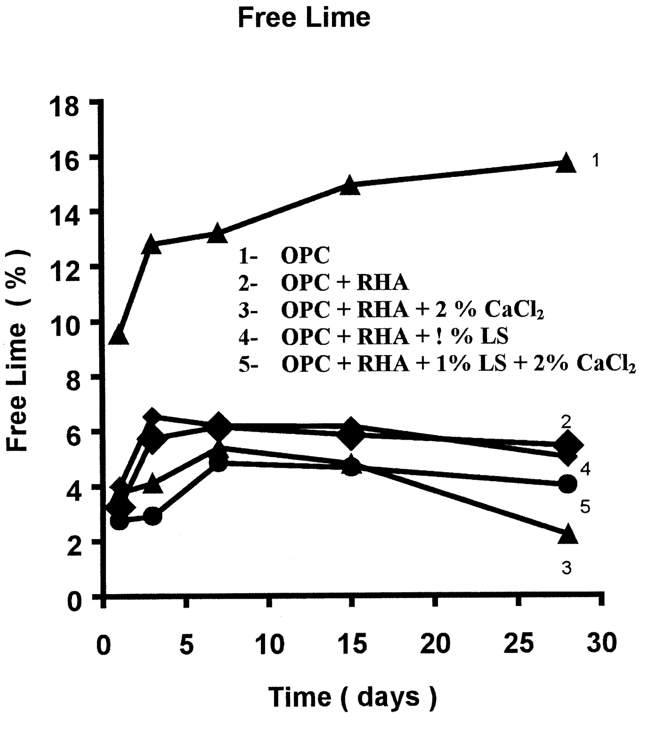

Fig. 3. Variation of free lime with hydration time in the presence of admixtures in the case of blended cement containing 10% RHA.

The analysis of the liquid phase has shown that as the time progressed, the Ca^{++} ion concentrations decreased in the liquid phase indicating that the hydration products have precipitated. The concentration of Ca^{++} ions in the presence of 2% $CaCl_2$ and in the presence of a mixture of 1% LS and 2% $CaCl_2$ is much higher than those in other cases. The reason is that excess of Ca^{++} ions are there due to $CaCl_2$.

The hydroxide ion concentration in the liquid phase increases with hydration time in all the cases. The increase in hydroxide ion concentration is a result of hydration reactions and the dissolution of alkali metal oxides present in the cement. For OPC, the values are the highest at all the times of hydration, whereas in the presence of RHA the values are lower as compared to that of OPC alone. This may be due to dilution effect as well as due to pozzolanic reaction. In the presence of 2% $CaCl_2$ or 1% LS, the values are almost the same indicating that hydroxides are precipitated or acceleration of pozzolanic reaction has occurred. However, in the presence of a mixture of $CaCl_2$ and LS the values are the lowest at all the times of hydration. It appears that two admixtures in combination either enhances the pozzolanic reactivity or precipitates larger amounts of hydration products as a result of which the hydroxide ion concentrations are decreased; however, the compressive strength measurements support the acceleration of pozzolanic reaction.

DTA curves of hydrated cements at 28 days of hydration have shown a broad endothermic peak at about 550 °C, which shows the decomposition of calcium hydroxide formed during hydration. The amount of calcium hydroxide formed is related to the area of this endothermic peak. The relative areas in the presence of different admixtures follow the sequence: OPC > (OPC + RHA) > (OPC + RHA + LS) > (OPC + RHA + LS + $CaCl_2$) > (OPC + RHA + $CaCl_2$). The results show that at 28 days of hydration the minimum amount of calcium hydroxide is formed in the presence of 2% calcium chloride, indicating that calcium chloride accelerates the pozzolanic reaction of RHA with calcium hydroxide obtained from the hydration of OPC. The results have also been supported by X-ray diffraction studies.

The IR spectra of OPC (anhydrous and hydrated for 1 day) and OPC–RHA blended cement hydrated for 1 day in the absence and presence of 2.0 wt.% $CaCl_2$, 1.0 wt.% LS, and mixture of the two admixtures are shown in Fig. 4. In the case of anhydrous OPC, bands at 452 cm^{-1} (ν_2) due to in plane Si–O bending vibrations, 522.2 cm^{-1} (ν_4) due to Si–O out of plane bending vibrations, and 921.6 cm^{-1} (ν_3) due to Si–O asymmetric vibrations of SiO_4^{4-} tetrahedra of the silicate phase present as di- and tricalcium silicate in the cement are observed. A very weak band at 874 cm^{-1} is also observed due to alite (C_3S) phase. The cement is partially hydrated due to atmospheric moisture and hence a very weak and broad band between 3300–3640 cm^{-1} due to O–H stretching and a weak band at 1684.1 cm^{-1} due to O–H bending vibrations are observed. The triple bands appearing between 1095–1150 cm^{-1} are due to S–O stretching vibrations (ν_3) of the SO_4^{2-} group of gypsum present in the cement. Weak bands in the range 638–675 cm^{-1} are due to bending (ν_2) vibrations of SO_4^{2-}. In spite of precautions, it is difficult to avoid atmospheric moisture and hence dry cement is always partially hydrated and as a result very small amounts of $Ca(OH)_2$ are also formed, which reacts with atmospheric CO_2 forming $CaCO_3$. Bands seen between 1425–1460 cm^{-1} are due to the CO_3^{2-} group. The band assignments are in good agreement with those reported in the literature [18,19].

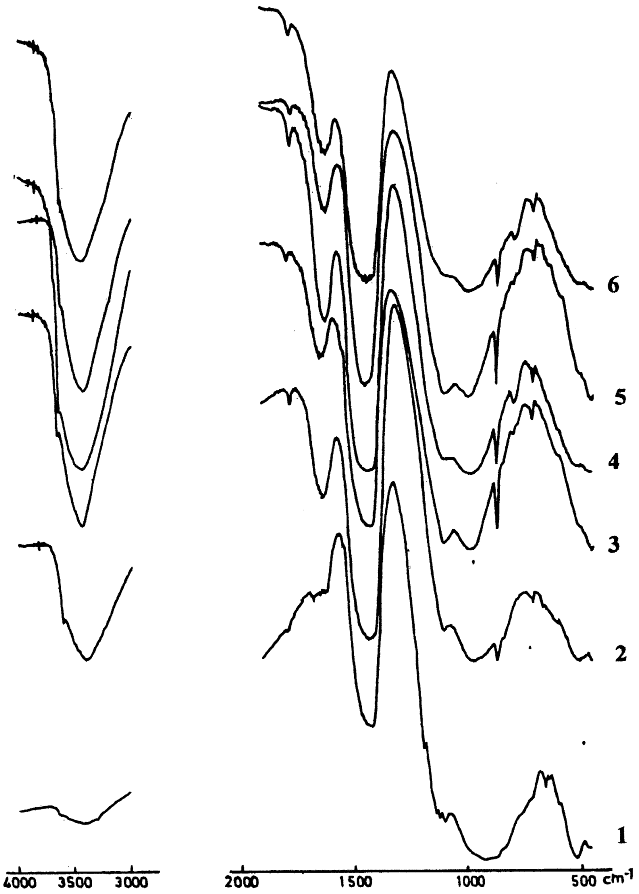

Fig. 4. IR spectra of cement hydrated for 1 day in the presence of admixtures: (1) OPC (anhydrous), (2) OPC (hydrated), (3) OPC + RHA, (4) OPC + RHA + 2% $CaCl_2$, (5) OPC + RHA + 1% LS, and (6) OPC + RHA + 2% $CaCl_2$ + 1% LS.

When OPC is allowed to hydrate for 1 day, some major changes are observed in the IR spectra. A band at ~3627.3 cm^{-1} is due to OH^- stretching vibrations of $Ca(OH)_2$ formed during hydration, whereas a broad and intense band at 3435.6 cm^{-1} is due to hydrogen bonded OH^- and the bending vibration also becomes strong and shifted to lower frequency (1652.1 cm^{-1}). Intensity of the carbonate band is increased and shifted to higher frequency. This is due to the increased amount of carbonate formed. The weak triple bands between 1095–1150 cm^{-1} seen in anhydrous cement due to SO_4^{2-} merged to a single sharp band at 1100 cm^{-1}, which may be due to the reaction of sulfate with C_3A phase. The Si–O asymmetric vibration is shifted to a higher wave number (975.3 cm^{-1}), indicating the polymerization of SiO_4^{4-} tetrahedra as a result of hydration. A weak band at 874 cm^{-1} in the case of anhydrous OPC becomes sharp due to the increased hydration of the alite phase [20].

The spectral features of the OPC–RHA blended cement hydrated for 1 day are almost similar to that of OPC hydrated for 1 day. However, the intensities of the bands are increased. The peak at 874.1 cm^{-1} is more pronounced and Si–O asymmetric vibration is shifted to 954.2 cm^{-1}, indicating higher degree of hydration.

In the presence of 2.0 wt.% $CaCl_2$ the intensities of the OH^- bands are much enhanced due to the higher degree of hydration and as a result silicate polymerization is increased and more C–S–H gel is formed [21].

In the presence of 1.0 wt.% LS the intensities of the peaks of OH^- bands are lower as compared to that in the presence of $CaCl_2$, indicating lower hydration. However, shifting of Si–O asymmetric vibration at higher frequency (999.1 cm^{-1}) indicates higher polymerization of silicate.

IR spectra of OPC–RHA blended cement hydrated for 1 day in the presence of mixture of admixtures (2.0 wt. $CaCl_2$ + 1.0 wt.% LS) shows that bands due to the OH^- group have the highest intensity as compared to other samples and the shift in Si 0–O asymmetric vibration is maximum (1003.9 cm^{-1}). The overall results show that the mixture of the two admixtures is acting as a strong accelerator for cement hydration.

The effect of 1% LS and 2% $CaCl_2$ on the compressive strengths at 7 and 28 days of hydration is shown in Fig. 5. The figure shows that in the presence of 2% $CaCl_2$ the compressive strength is higher at 7 days and lower at 28 days of hydration than that of control. In the presence of 1% LS, the values are lower than that of control on all days of hydration. However, in the presence of a mixture of 1% LS and 2% $CaCl_2$ the compressive strength is maximum at 28 days of hydration. The results very clearly show that when a mixture of a superplasticizer (1% LS) and an accelerator (2% $CaCl_2$) is added to the RHA-blended OPC, the superplasticizer reduces the water demand and the accelerator enhances the compressive strength and thus the role of the two admixtures becomes supplementary to each other.

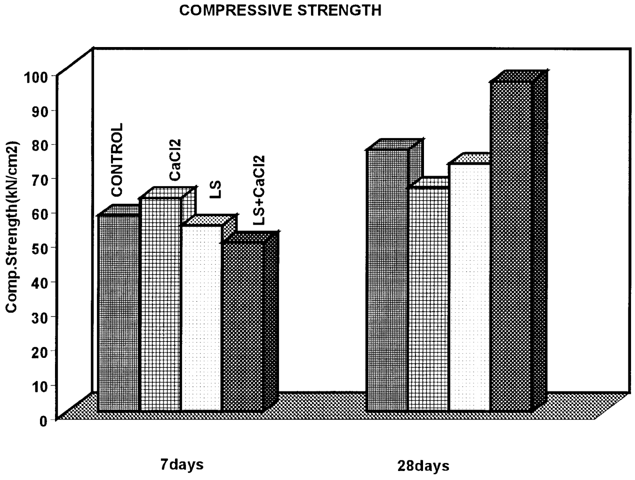

Fig. 5. Effect of admixtures on the compressive strength of blended cement at 7 and 28 days of hydration.

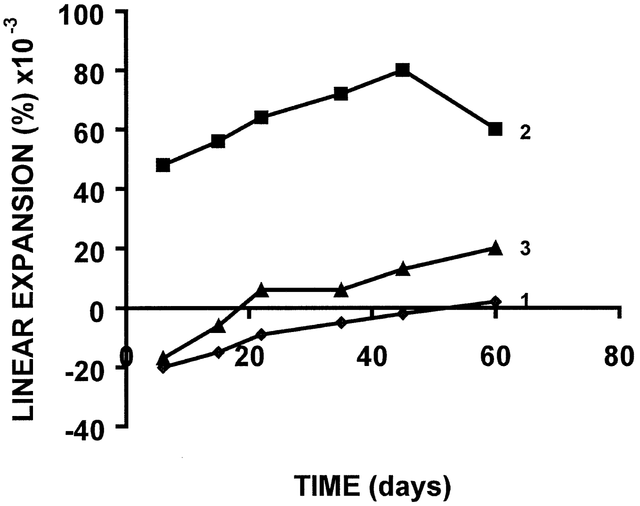

Fig. 6. Linear expansion of blended cement hydrated in the presence of admixtures in N/60 sulfuric acid. (1) Blended cement (control), (2) blended cement (2% $CaCl_2$), and (3) blended cement (2% $CaCl_2$ + 1% LS).

The scanning electron microscopic analysis of 10% RHA-blended OPC hydrated for 28 days in the presence of a mixture of 2% $CaCl_2$ and 1% LS has shown that the structure is more compact. It appears that LS reduces the water requirement and calcium chloride accelerates the hydration process, which results in the development of a compact structure leading to higher compressive strength. This is in agreement with the compressive strength results.

The effect of aggressive atmosphere (N/60 H_2SO_4) on the linear expansions of bars (28 × 2.5 × 2.3 cm) is shown in Fig. 6. The percent linear expansion increased with the time of exposure in all cases but the values are the lowest for the control (blended cement) and highest in the presence of calcium chloride. However, in the presence of a mixture of 1% LS and 2% calcium chloride the values are in between that of control and calcium chloride. It may be due to the chemical interaction between $CaCl_2$ and C_3A, making Friedel salt. It may also be due to the complex chemical reaction between H_2SO_4, $CaCl_2$, and the hydration products, leading to dissolution, leaching, and expansive salt formation [22,23]. It appears that control (blended cement) is more resistant to the aggressive atmosphere than those in the presence of calcium chloride or a mixture of calcium chloride and LS. The results suggest that calcium chloride accelerates the corrosion of the cement.

4. Conclusions

The results have shown that the compressive strength of 10 wt.% RHA-blended portland cement is maximum in the presence of a mixture of 2 wt.% $CaCl_2$ and 1% LS. It has also been confirmed by FTIR spectral studies. However, the results on corrosion studies have shown that RHA-blended cement without any admixture ($CaCl_2$, LS, or both) is more resistant to the corrosive atmosphere of N/60 H_2SO_4.

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