

# Chemical and Thermal Activation of Sodium-Rich Calcium Alumino-Silicate Binder

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## Abstract

The aim of the present paper is to evaluate the potential conversion of a chemically- and thermally-modified sodium-rich calcium alumino-silicate material (SRCAS, the engineering product of a treated waste product from the aluminium industry, spent pot-liners) into a new binder. Thus, great savings could be made due to the dual nature of SRCAS both as a mineral admixture and as a clinker-free binder. This paper presents the results of an investigation into the use of appropriate activators and/or favourable activation conditions (humidity, temperature) to further improve the binding properties of SRCAS. Effective activators (type and concentration), temperature of activation, and water-to-binder ratio were evaluated. Experimental results show that SRCAS has been easily transformed into a binder from which different paste, mortar, and concrete have been successfully fabricated and tested. High early-strength paste, mortar, and concrete have been obtained after less than 24 hours and some pastes have resulted in compressive strengths of 90MPa after the same activation time.

## 1. Introduction

Finding an economical method of converting industrial by-products and engineered materials into ecological binders is of great importance. Since the middle of this century, a new technology for converting such materials into ecological binders has been applied to real construction. Some researchers have succeeded in activating these materials and finding the suitable building applications [1-5].

This paper presents the results of investigating the use of appropriate activators and/or favourable activation conditions (humidity, temperature) to improve the binding properties of sodium-rich alumino-silicate (SRCAS) material. SRCAS is an amorphous material that has been successfully used in different applications as an alternative supplementary cementing material [6]. The production process of SRCAS has been shown by Laldji and et al. [7].

To begin the activation process, a threshold concentration value for each activator must be established, before which insignificant activation takes place. At this threshold concentration, there may also be a need for a

certain quantity of energy to overcome the initial activation energy barrier needed to start the activation process. Optimum combination of chemical and thermal (chemo-thermal) activation may lead to favourable results.

Therefore, the objective of this study is to investigate cementitious properties of SRCAS, and select the best activator and temperature of activation. As well, the secondary objective is to find the optimum binder-to-aggregate ratio that gives significant mechanical properties. Microstructure analysis was performed on the activated pastes to understand the mechanism of binder-activator reaction.

## 2. Materials

### 2.1 Physical and chemical compositions of the materials used

The chemical composition of SRCAS analyzed by X-ray fluorescence (XRF), as well as density and fineness, are shown in Table 1.

Table 1. Chemical composition and physical properties of SRCAS.

	SiO <sub>2</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	CaO (%)	MgO (%)	Na <sub>2</sub> O <sub>eq</sub> (%)	CaF <sub>2</sub> (%)	Density (g/cm <sup>3</sup> )	Fineness (m <sup>2</sup> /kg)
SRCAS	33.80	25.10	3.40	14.60	0.76	10.12	12.1	2.85	419

Technical grade lime (CH) and sodium hydroxide as a strong base (SB) were used as activators.

## 3. Experimental program

### 3.1 Strong base (SB) activator

#### 3.1.1 Mixing procedures

The mixing of paste was carried out in a 5-liter stainless steel mixing bowl. The total amount of binder used for any given batch ranged from 1.25 to 2.5 kg. Mixing was conducted using a two-speed mixer. Pastes were prepared by mixing the pre-weighed SB, mixing water in the mixing bowl, and then adding the pre-weighed SRCAS powder to this solution and mixing for 2 minutes at slow speed. Meanwhile, the mixing was stopped for 2 minutes. Finally, mixing was performed for another 2 minutes at high speed. In the case of mortar, the sand was added after the addition of binder over 30 seconds at low speed, and then blended for 2 minutes at high speed. The resulting paste or mortar was then cast in molds measuring 50 × 50 × 50 mm.

The molds were placed 5 cm above the water at the bottom of the curing chamber, after which the chamber was vapor saturated. The samples were supported over the water by means of a steel rack with four vertical support legs. The temperature was automatically controlled through an electronic unit attached to an LCD screen with an electronic recorder to register temperature change with time. In this reactor, the temperature

was kept constant. The relative humidity during the activation process was maintained at about 100% R.H. The total curing time used in this study was 18 hours. Three temperatures of activation of 50, 60, and 80°C were used in paste mixtures. The activation of mortar was performed at 60°C. After steam curing, the molds were removed from the reactor and covered with a thermal insulator to cool down slowly. At the end, samples were demolded and cured in the humidity chamber (20±2°C and 100% R.H.) until they reached testing time. The pastes were tested for compressive strength at 1, 7, and 28 days, while the mortars were tested at 1, 7, 28, and 91 days of curing. The compressive strength is the average of 3 tested samples.

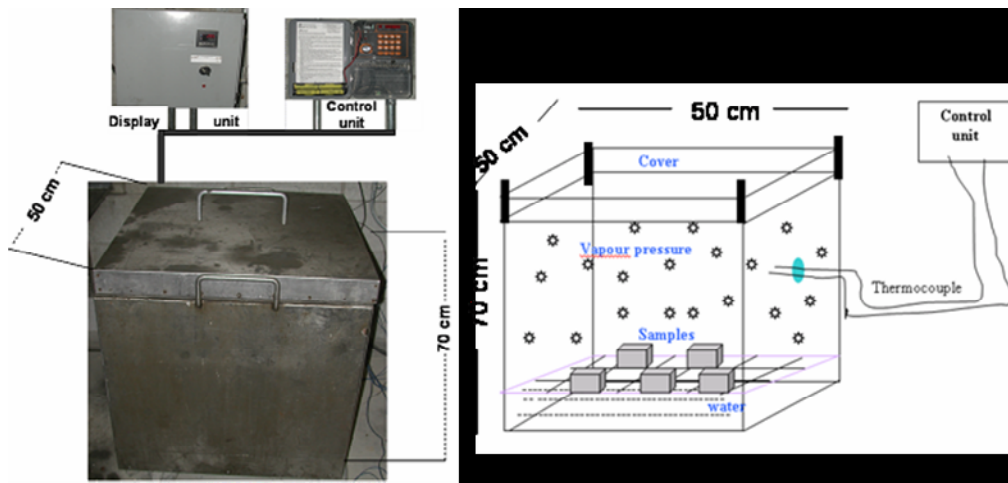


Figure 1. Picture and diagram of the curing chamber

### 3.1.2 Mix designs

#### Paste mix design

A constant SRCAS content was used, and the water-to-binder ratio (w/b) was changed depending on apparent workability (the paste should be easily poured in the moulds), which depends on SB concentration, as shown in Table 2. The molar concentrations of SB were calculated with respect to the added water. Different SB molar concentrations were referred to as C1 to C5, as shown in Table 2.

Table 2 Mixture characteristics of the pastes tested at 50, 60, and 80°C

Symbol	SB concentration (mol)			W/SRCAS
	50°C	60°C	80°C	
C1	0,52	0,51	0.556	0.307
C2	1,05	1,01	1.054	0.308
C3	1,53	1,52	1.603	0.415
C4	2,03	2,02	2.110	0.322
C5	2,49	2,53	2.618	0.312

C1 to C5 stand for different SB molar concentrations

### Mortar mix design

The mortar mix design was calculated at different ratios of (SRCAS/(SRCAS+sand)) so as to determine the optimum binder-to-sand ratio that gives the highest compressive strength. This optimum ratio will be used in the concrete mix design. Ottawa sand was used. A flow value of 25±5 cm was chosen as the target flow, as shown in Table 3. The selected SB concentration is based on results obtained from pastes.

Table 3. Mixture characteristics of the mortar samples tested at 60°C

SRCAS/(SRCAS+sand) %	W/SRCAS	SB (mol)	Flow (cm)
66.67	0.343	1.41	30.0
50.00	0.344	1.41	28.5
40.00	0.348	1.39	26.0
33.33	0.365	1.32	21.5
28.57	0.415	1.17	22.0

### 3.2 Reaction of SRCAS with lime (CH)

A mixture of 80% dry SRCAS powder and 20% hydrated lime was produced. This mixture was mixed with water (SRCAS-to-water ratio was 0.40) and the paste was cast in molds measuring 50 × 50 × 50 mm and cured at 80°C in 100% R.H. for 18 hours in the curing chamber. After steam curing, the moulds were removed from the curing chamber and covered with a thermal insulator to cool down slowly. The samples were then tested for compressive strength. The compressive strength was the average of 3 tested samples. Paste hydration was also monitored by X-ray diffraction (XRD) analysis.

### 3.3 Concrete

Three concrete mixtures (M1, M2, M3) were prepared based on paste and mortar results. It is important to mention that M1 and M2 were prepared using different mixtures of CH and SB, while M3 was prepared using only CH, as shown in Table 4. Siliceous sand and limestone coarse aggregates

were used in concrete. A Polynaphthalene sulfonate where used as superpalsticizer

Table 4 Mix design for different activated concrete mixtures

Concrete mix design (1 m3)				
Materials	Density g/cm <sup>3</sup>	M1	M2	M3
SRCAS (Kg)	2.85	451.2	451.2	427.36
Water (Kg)	1.00	168.0	178.0	206
W/SRCAS	-	0.37	0.39	0.39
Sand (kg)	2.69	712	712	712
Coarse aggregate (14mm) (kg)	2.69	1100	1070	894
SB (%)	-	2.0	3.46	-
CH (%)	2.24	0.18	0.55	24.5
SP, dry extract (%)	-	0.12	0.08	0.71

### 3.3.1 Concrete mixing procedure

SB activator was dissolved in mixing water, while CH was pre-weighed with SRCAS powder. The fine aggregate was added to the stationary drum mixer first. The coarse aggregate ( 14 mm) was then added to sand within 30 seconds during the rotation of this drum mixer. Meanwhile, half the amount of mixing water was added, followed by the binder, leaving the drum under rotation for 2.5 minutes. It was then stopped for another 2.5 minutes, after which it was left to rotate for another 4 minutes. The concrete was cast in 100 x 100 mm cylindrical moulds. The moulds were then placed in a curing chamber (Figure 1) and cured for 18 hours at 70°C. After steam curing, the moulds were removed from the reactor and covered with a thermal insulator to cool down slowly. At the end, cylinders were demoulded and cured in the humidity chamber (20±2°C and 100% R.H.) until they reached their testing times. Concrete cylinders were tested for compressive strength at 1, 7, 51, and 850 days. The compressive strength was the average of 3 tested samples at each age.

## 3. Results and discussion

### 3.1 Reaction of SRCAS with strong base (SB)

#### 3.1.1 Pastes

At a curing age of 1 day and at each concentration of SB, the compressive strength increases with an increase in temperature ranging from 50 to 80°C. As well, at any temperature, compressive strength increases as the concentration of the activator increases. In addition, higher compressive strengths were obtained at a higher concentration, as shown in Figure 2, while at 7 days, a significant reduction in compressive strength was observed. The optimum concentration of SB activator at 50, 60 and 80°C

seems to be at concentrations of C3, C1 and C2% SB, respectively, as shown in Figure 2. This optimum value is based on the minimum concentration of SB, which has a significant effect on compressive strength. At a curing age of 28 days, there are two optima at 60°C with concentrations of C1 and C4% SB, while at 50°C there is only one optimum concentration at C5% SB. As well, at 80°C there is only one optimum concentration at C2% SB, as shown in Figure 2. Variations and loss in compressive strength can be interpreted by the synergistic effect of temperature and SB concentration. Increase of temperature shifts the effective SB concentration from higher to lower value. In order to show this phenomenon clearly, a statistical analysis was performed.

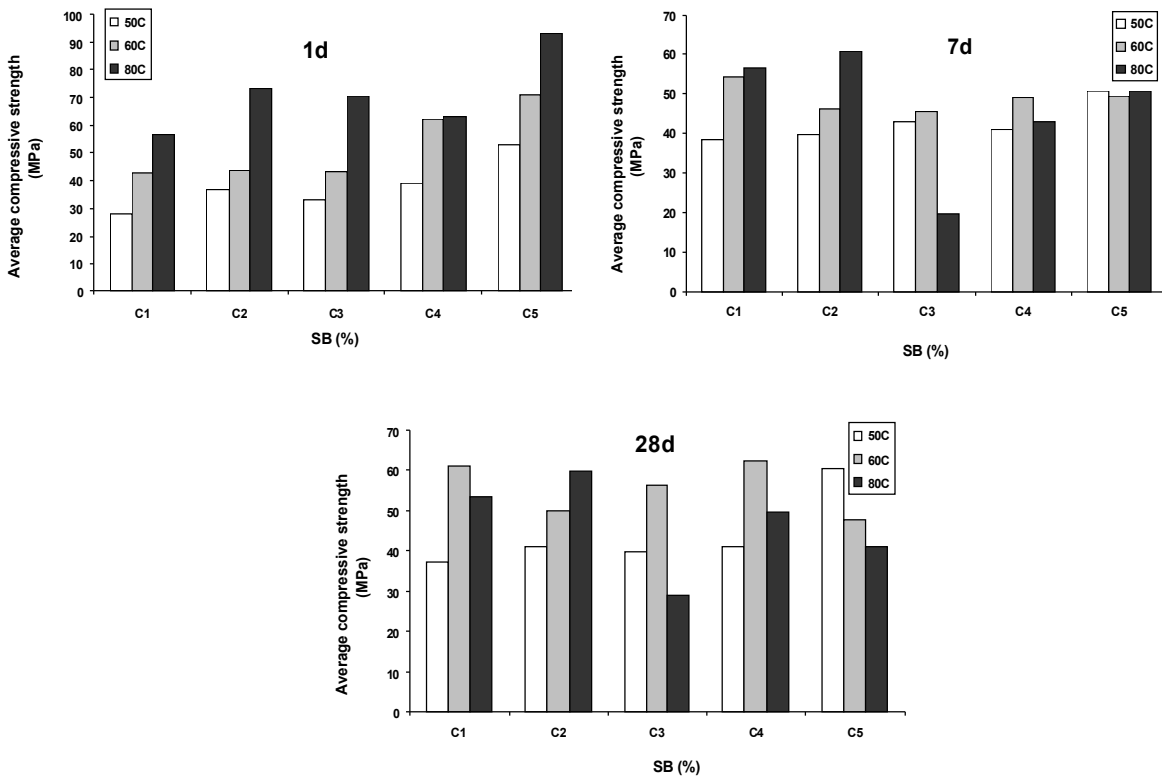


Figure 2. Comparison between mixtures activated at different temperatures (50, 60, and 80°C) and concentrations of activator at 1, 7, and 28 days.

### Statistical analyses

Simple statistical analysis was carried out from the previously mentioned results to calculate the rate of gain in compressive strength with temperature at constant SB concentration and curing age. The analysis was performed using results obtained from 1-day curing. Using regression and best-fit line analyses, the following equations, shown in Table 5, were obtained:

Table 5. Equations for best-fit lines of compressive strength-temperature relation

Concentration	Best fit equations	R <sup>2</sup> =
C1	$F_{C_1} = -0.026 * T^2 + 4.3435 * T - 124.16$	1
C2	$F_{C_2} = 0.025 * T^2 - 2.0232 * T + 75.16$	1
C3	$F_{C_3} = 0.0112 * T^2 - 0.2108 * T - 15.6$	1
C4	$F_{C_4} = -0.0511 * T^2 + 7.9493 * T - 231.18$	1
C5	$F_{C_5} = -0.0236 * T^2 + 4.3923 * T - 107.7$	1

F<sub>c</sub> stands for the compressive strength, C for concentration and T for temperature.

From Table 5 the first derivative equation at each concentration was obtained and used to determine compressive strength gain at each temperature (50, 60, and 80°C). This gain in compressive strength is presented in Figure 3. It is clear from Figure 3 that at 50°C, the optimum concentration is the highest (C4 and C5), while when the temperature was increased to 60°C, the effectiveness of the low concentration significantly improved (C2 and C3). At a high temperature of 80°C, the optimum effective concentration was shifted to lower values (C2 and C3). The explanation as to why at 80°C and higher SB concentration, compressive strength experiences an abrupt drop was attributed to the formation of villiumite mineral (NaF), as shown in XRD and SEM-EDS analyses.

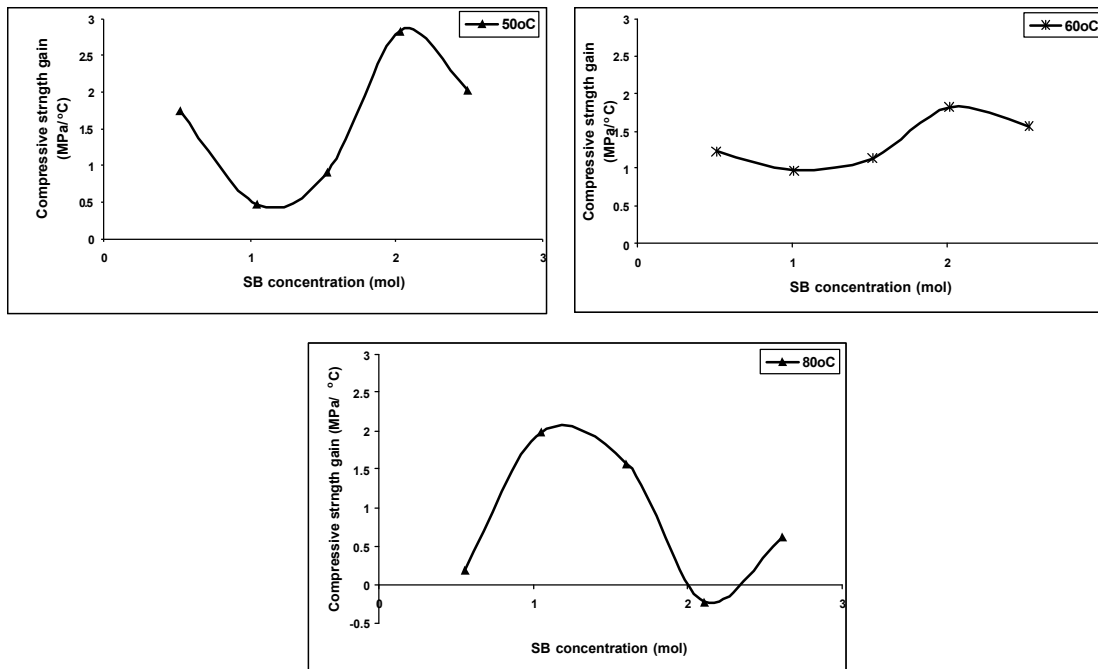


Figure 3 Change in the rate of gain in compressive strength at different SB molar concentrations and different temperatures of activation

### XRD and SEM-EDS analyses

A series of XRD and SEM-EDS analyses were undertaken to interpret the mechanism of activation. XRD analysis has been performed on the sample activated at 80°C for 24 hours and identified as C1, C2, and C5% SB, as shown in Figure 4. XRD analysis showed the presence of villiaumite mineral (NaF), which is very soluble under the curing condition applied (100% R.H.). NaF formation should lead to instability of the cementitious system formed [8-10]. The formation of NaF increases with an increase in SB concentration. The fluoride itself is present in SRCAS composition, as shown in Table 1. NaF formation leads to a significant reduction in compressive strength. Notable surface deterioration was observed in the form of a cleavage, accompanied by splitting and cracks. This may also explain the previously mentioned reduction in compressive strengths of pastes at 80°C. NaF formation was overcome by adding CH activator to SCRAS mixture to form fluorite mineral (CaF<sub>2</sub>), which is more stable than villiaumite, as shown later in Figure 7, while the XRD analysis shows zeolite-like crystal formation. SEM-EDS analysis was performed on SRCAS pastes activated at 50°C for 18 hours. SEM-EDS analysis showed the effect of SB concentration on the particle surface of SRCAS. As well, it shows the formation of zeolite-like crystals, as confirmed by XRD analysis, shown in Figures 4, 5, and 6.

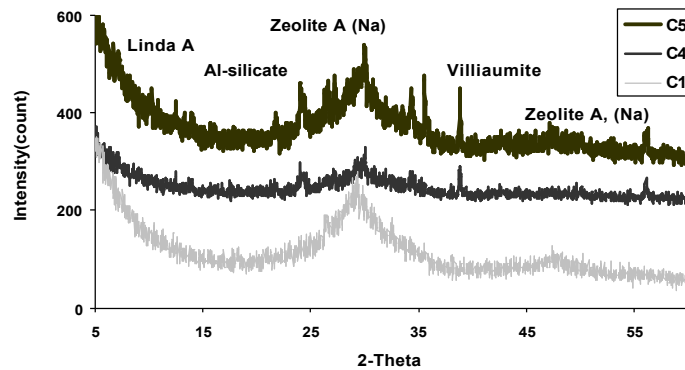
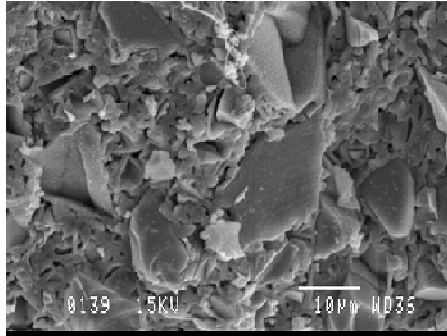
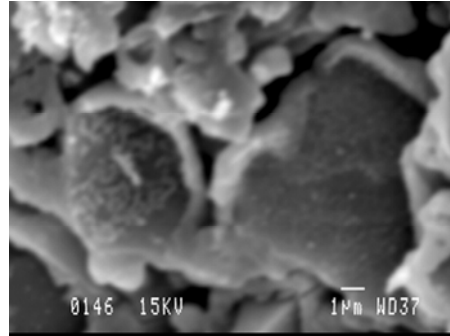


Figure 4. XRD analysis of the activated SRCAS pastes using different SB concentrations





a) SEM image of SRCAS paste, activated by C1% SB at 50°C, for 18 hours.



b) SEM image of SRCAS paste, activated by C2% SB at 50°C, for 18 hours.

Figure 5. SEM photomicrographs of the activated SRCAS pastes

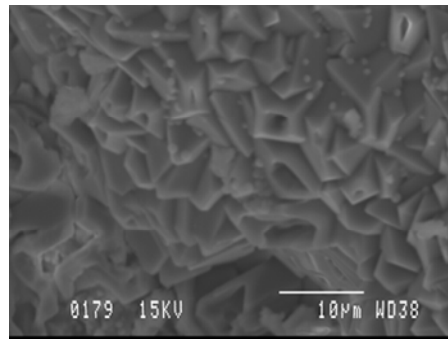
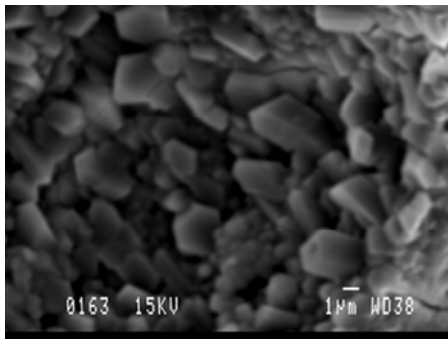


Figure 6. SEM photomicrographs of the activated SRCAS paste samples at 50°C and C5% SB showing zeolite-like structure formation

### 3.1.2 Mortar

Different mortars were made using SB activator so as to determine the optimum binder-to-sand ratio. A temperature of 60°C was chosen as the optimum temperature of activation based on results obtained from pastes. The effect of sand-to-SRCAS ratio on compressive strength is shown in Figure 6. The optimum SRCAS/(SRCAS+sand) was found to be 40%, where the water-to-SRCAS ratio was 0.348 and the molar concentration of SB was 1.39 molar, as shown in Table 3. The optimum SRCAS/(SRCAS+sand) reflects the strength of the bonding force between the newly formed cementitious phases and sand.

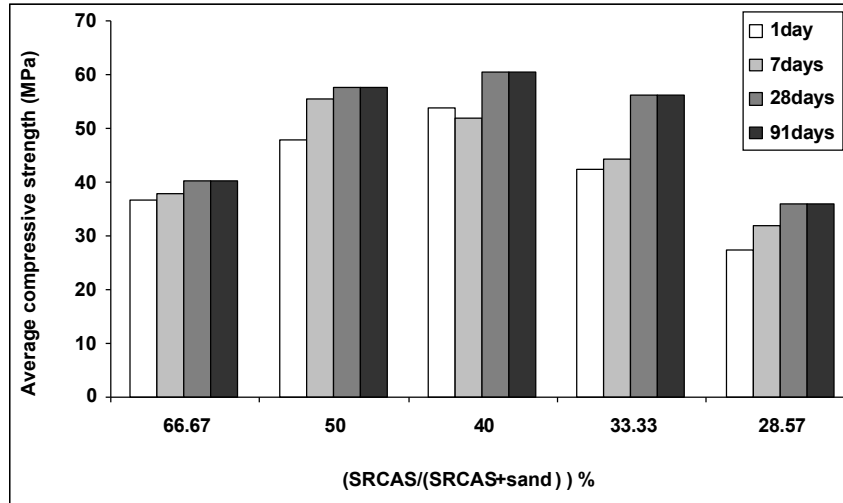


Figure 6 Compressive strength of mortar for 1, 7, 28, and 91 days activated at 60°C.

Furthermore, Figure 6 shows that there is continuous strength gain up to 28 days, which then stabilizes with time until 91 days.

### 3.2 Reaction of SRCAS with lime

X-ray diffraction analysis has effectively shown that after 18 hours of hydration, the lime was almost completely consumed (Figure 7). This test showed the strong pozzolanic behavior of SRCAS. Figure 4 has also shows the formation of fluorite (CaF<sub>2</sub>). Fluorite is a stable mineral. Although, part of the lime was used in fluorite formation, the pozzolanic behavior of SRCAS is still predominant because the compressive strength of the paste was found to be about 16 MPa after 18 hours.

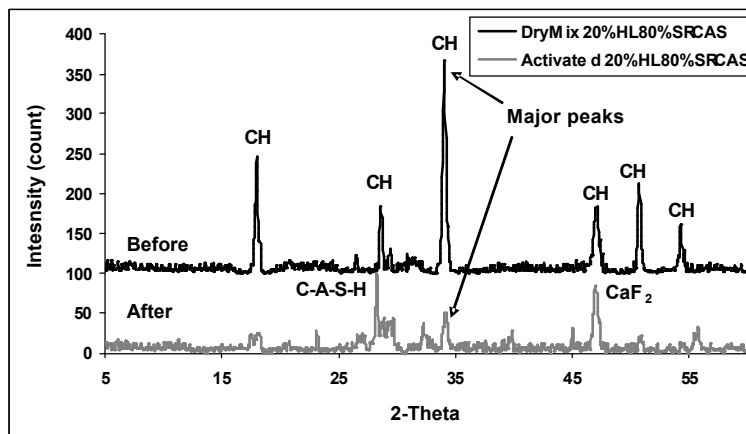


Figure 7. XRD analysis of SRCAS mixture before and after hydration

### 3.3 Concrete

The concrete mixtures whose compositions are shown in Table 4 were activated in the same reactor shown in Figure 1. The results obtained have shown the effectiveness of SB activator, as presented in Figure 8. The compressive strength obtained was stable up to 51 days, after which there is a gradual increase up to 850 days. The maximum compressive strengths given by M1, M2, and M3 were 35, 51, and 40 MPa, respectively, as shown in Figure 8. The concrete mixtures of M1 and M2 were activated by binary mixture of SB and CH, while M3 was activated by CH, as shown in Table 4. It is important to note that CH content of M3 was very high (24.5%) in comparison with M1 and M2 (0.18 and 0.55%, respectively). Therefore, this highlights the effectiveness of SB activator.

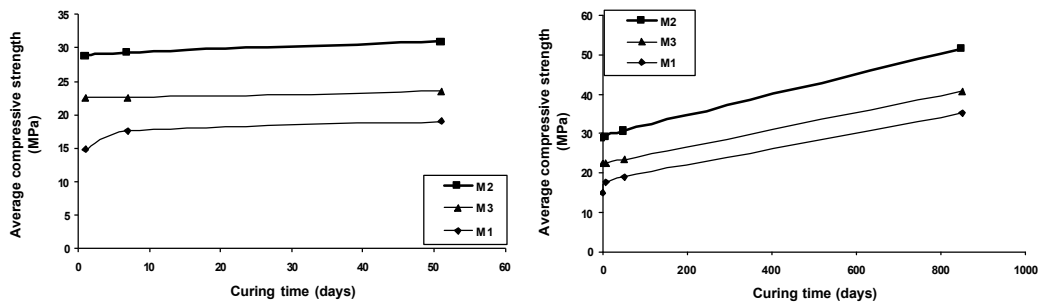


Figure 8. Average compressive strength of concrete mixtures at short and long term.

### 4. Assumptions related to reaction mechanism

In the present research, and according to the results obtained, especially from the microstructural analysis, a simple mechanism was assumed. Under fixed fineness, there is a threshold concentration value for each activator at which there is significant change taking place on the surface of the particle. This change depends on activator concentration and temperature of activation. Under the effect of activation conditions (temperature, activator concentration, and humidity), there is dissolution of the aluminate and silicate network at the surface of SRCAS particles. Subsequently, aluminosilicate gel, and later zeolite, are formed, leading to a dense cementitious matrix.

### 5. Conclusions

It is evident that SRCAS, a cementitious material, can be converted into a new economical binder. Better understanding of the physical and chemical behavior of SRCAS was achieved. The chemical composition of SRCAS gives a good idea of the reaction product. SB is an effective activator whose effectiveness increases with temperature. A temperature of 60°C seems to be the optimum for SRCAS activation. Higher temperatures are not recommended. A low concentration of SB, depending on the temperature of activation, is also recommended to avoid the formation of a

significant amount of villiaumite, which negatively affects the mechanical properties of SRCAS paste.

## 6. References

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