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Synopsis: This paper presents new materials obtained by alkaline activation, which generally have a lower environmental impact than that based on hydraulic binders. Calcareous filler was alkali activated by sodium hydroxide solutions in mortars prepared with siliceous sand. The chemical, physical and mechanical properties were studied after 28 days curing. XRD showed that setting and hardening processes of the binder result from the crystallization of sodium/calcium carbonate hydrate (pirssonite) and calcium hydroxide (portlandite). Depending on the formulation parameters, the compressive strength reached, after 28 days, 20 MPa [2900 psi] while flexural strength reached 4 MPa [600 psi]. A methodology, based on thermal analysis results, was applied to quantify the formed products and to evaluate the reagents consumption extent. Calculated amounts had a high reliability and corroborated the initial composition of the mortars. These results open interesting possibilities to improve the performances of these new type materials, based on alkali-activated calcareous filler.

Keywords: alkali-activation, compressive strength, flexural strength, limestone filler, pirssonite, thermal analysis.

INTRODUCTION

Materials obtained by alkaline activation, compared with traditional cement-based building materials, offer a very promising alternative for significantly reducing the CO₂ balance and the environmental impact of the construction industry [1-2]. Much progress was observed last years in this field with the development of geopolymers [3], obtained by alkaline activation of silicoaluminous components such as fly ash [4], metakaolin [5], blast furnace slag [6], but also recycled concrete powder [7] or clays [8]. The activation, with alkali silicates and hydroxides of sodium or potassium, leads progressively to a polymerization forming, after dissolution of the silicates and aluminates, an amorphous gel of alkali silico-aluminates and, sometimes, nano zeolite crystals. Despite the growing interest for alkali-activated materials, very few researches have focused on alkaline activation of calcareous compounds and the main studies concern mixtures containing active silicate compounds. A patent, related to storing wastes, proposed a way to produce solid material from activation of calcareous compound and sodium oxide by alkali metal hydroxide in the presence of water and waste [9]. This mix, after few days or weeks at room temperature without additional thermal energy, leads to a new solid material composed of Tobermorite $(Ca_5Si_6O_{16}(OH)_2.4H_2O)$, Pirssonite $(Na_2Ca(CO_3)_2.5H_2O)$ and Gaylussite $(Na_2Ca(CO_3)_2.5H_2O)$ but nothing was mentioned about their strengths. A study [10] focuses in the production of new binders based on glass waste and/or limestone activated by sodium hydroxide (NaOH) and/or carbonate sodium (Na₂CO₃). This binders were prepared with a mass ratio CaO/SiO₂ = 0.5 (based on the proportion and composition of the glass and limestone used); a water/binder ratio of 0.3; preactivation of the precursors; an alkaline activator composed of a mixture of Na₂CO₃/NaOH and hardening in an isothermal chamber maintained at 40°C [104°F]. The main products of the reaction are amorphous calcium silicate hydrates (C-S-H), silica gel and crystalline phases as pirssonite, gaylussite and portlandite (Ca(OH)₂). A compressive strength of 32.3 MPa [4641 psi] at 28 days was obtained. The presence of sodium hydroxide in the activator promotes the formation of pirssonite and reduces that of C-S-H but glass waste reacts more intensely with sodium hydroxide. Another study [11] activates limestone by sodium silicates solutions and sodium hydroxide adjusting the SiO₂/Na₂O molar ratio to 0.1 and 1.5. After 360 days at 20°C [68°F], the compressive strength obtained on the mortars can reach 14 to 24 MPa [2000 to 3500 psi]. The reaction process starts with the hydrolysis and dissolution of the limestone particles causing the formation of Ca²⁺ and CO_3^{2-} ions in the aqueous medium which react with the $SiO_x(OH)_{4-x}$, Na⁺ and OH⁻ ions of sodium silicate [12]. The formed species becomes more and more complex over time, saturate the aqueous medium to form various reaction products: calcium silicate hydrate (C-S-H), calcium silicate hydrate incorporating sodium (N-C-S-H), sodium silicate hydrate (N-S-H) and carbonate finely intermixed. The presence of sodium hydroxide in the activation solution leads to the formation of carbonate minerals: Thermonatrite (Na₂(CO₃).H₂O) and pirssonite. These products have two contradictory effects on the microstructure of the matrix. They cause the reduction of the porosity, improving the compressive strength, but on the other hand, they occupy a larger volume than the original hydroxides, which, in the presence of humidity, would generate internal stresses and loss of mechanical strength.

In this study, we are interested in a new system, which differs from those presented above [9-12] in particular, by its number of compounds. The system use only two compounds: calcareous filler and sodium hydroxide. There is no addition of active silicate phases. This field was only been previously approached in a work carried out in our laboratory. The developed materials presents binding capacities and water plays the same role as in cementitious materials (i.e. the increase of water content increase the workability but decrease the strength) [13]. Our aim is to describe and better understand the reaction process associated to alkaline activation of calcareous components and confirm the binding capacities of these new binders.

Materials

EXPERIMENTAL INVESTIGATION

The calcareous compound used in this study was a pure limestone filler (CaCO₃ = 98.3%) commonly used as an addition in concrete according to the NF P 18-508 standard [14]. Calcite (JCPDS 05-0586) was the only crystallized mineral identified by XRD (see XRD description for analysis conditions) and 97% of the particles were smaller than 63 μ m [0.0025 in.]. Table 1 summarized the main physical and chemical characteristics given by the supplier.

Standardized sand (Table 1), in accordance with EN NF 196-1 [15] and ISO 679 [16], was used for the preparation of mortars. Its composition was meanly siliceous according to information given by the supplier (Table1: SiO₂ 96.2%). The identification by XRD revealed a mineralogical composition based on crystallized quartz (JCPDS 46-1045) which was considered weakly reactive with sodium hydroxide. The particle size distribution was regular between 0 and 2 mm [0 and 0.0787 in] and the particles were round-shaped. The density and absorption coefficient were 2640 kg/m³ [165 lb/ft³] and 0.2%, respectively.

The activator used in this study was a solution of sodium hydroxide (NaOH) at 13 mol/L [10000 mol/yd³] obtained by dilution of concentrated soda solution 50 %_{wt} (i.e. 19 mol/L [14615 mol/yd³]) with a density of 1.515. The pH of the solution was around 15. All materials were maintained, in climatic chamber at 20°C [68°F] at least for 24 hours before mixing.

Specimens' preparation

Two compositions of mortar containing three parts of standardized sand and one part of limestone filler were prepared with two different proportions of soda solution so as to obtain a W/S ratio equal to 0.13 and 0.12. W was the mass of water and S was the total mass of solid compounds including limestone, sand and solid sodium hydroxide (in the solution). These compositions, named respectively "Na0.13" and "Na0.12" were presented in Table 2. Different batches were made for each composition and were named "Bn" where n referred to the number of the batch. Prismatic specimens 40x40x160 mm [1,5x1,5x6,33 in.] were prepared according to the standard EN NF 196-1 [15]. They were casted in two layers vibrated for 30 seconds each to release residual air bubbles. To minimize water evaporation at early ages, the molds were sealed in plastic bags. After 3 days, the samples were demolded and then cured in a two-step curing: 11 days sealed in plastic bags and 14 days dried at 45°C [113°F]. This drying was necessary to eliminate the free water and stabilize soluble products formed by the reaction. The real proportions of each batch were determined from accurate amounts put in the mixer (Table 3).

Tests methods

Monitoring of specimens weight loss was performed from demolding and throughout the curing time by weighing once a day, expressed in percentage of the initial mass (after demolding). This made possible to ensure that the mass of the samples was stabilized at the end of drying, before carrying out the following characterizations.

Flexural and compressive strength of cured samples were performed at 28 days according to standard NF EN 196-1 [15]. The values of flexural and compressive strength result were the mean value of, respectively, three and six individual tests.

Porosity measurements, in accordance with standards EN NF 1936 [17] and NF P18-459 [18] were carried out using ethanol instead of water in order to avoid possible dissolution of alkali-activation products. The porosity (P) was calculated from equation (1) and dry density of mortars (d) from equation (2).

$P = 100 \mathrm{x} \frac{m_{sat} - m_{dry}}{m_{sat} - m_{dry}}$	(1)
$m_{sat} - m_{Eth}$	
$d = d_{Eth} \frac{m_{afy}}{m_{sat} - m_{Eth}}$	(2)

where, m_{dry} was the dry mass of the samples at the end of the curing, m_{sat} was the mass of the cured samples ethanol saturated, m_{Eth} was the apparent mass of the cured samples, ethanol saturated, immersed in ethanol and d_{Eth} was the ethanol density.

For mineralogical characterization tests, representative pieces of specimens were collected after compression tests, crushed in less than 0.315 mm [0.0124 in] powder, then, sealed in plastics bags until the completion of XRD and DTA-TGA tests. XRD analysis was carried out with a copper anode ($\lambda_{(K\alpha)}$ =1.540598 Å [4x10⁻⁹ in.]). Scans were run with a step size of 0.0167° and a counting

time of 0.5715 s/step from 5° to 70° 20. DTA-TGA tests were carried out from 25°C [77°F] to 1100°C [2012°F] with a heating rate of 10°C/min [50°F/min] under dynamic nitrogen atmosphere (50mL/min [$6.54x10^{-5}$ yd³/min]). All the tests were performed by using approximately 110 mg [$24x10^{-5}$ lb] of sample. The results enabled us to identify and quantify the products formed in the mortar. The working hypotheses and the calculation method will be presented and discussed in the next section.

Kinetics of the alkali-activation during the first hours was characterized by semi-adiabatic calorimetry experiments [19] in a controlled temperature room maintained at 20 ± 0.2 °C [68 \pm 32°F]. Both mortar compositions were prepared using mechanical mixing for the sand and the filler during 30 s and hand-mixing during 1 min and 30 s after soda solution introduction directly into the steel vessel of the calorimeter. Then, the steel vessel was immediately put in the calorimeter and temperature was recorded.

RESULTS AND DISCUSSION

Kinetics of reaction

Figure 1 shows the heat of hydration of both compositions "Na0.13" and "Na0.12". Only two phases were identified. There were not dormancy, acceleration and equilibrium phases as in cementitious mortars [20]. The first (I), exothermic and very fast (about 2 and 5 minutes for Na0.12 and Na0.13, respectively), may be attributed to a phenomena of dissolution/precipitation of limestone. During the second phase (II), the measured heat slowly decreases and tends to stabilize. This phase could be linked to an evolution of the chemical arrangement of the system, but this point remains to be verified by additional measures for very young ages. Monitoring over longer times indicated asymptotic deceleration of this phase. The main difference between mortars Na0.12 and Na0.13 in terms of reaction heat and in reaction kinetics were related to the soda solution amount (i.e. quantities of water and solid sodium hydroxide). By increasing the solid sodium hydroxide (Na0.13), the heat of reaction increased, but at the same time, the increasing amount of water slowed down the dissolution kinetics. Similar results were obtained during the alkaline activation of slag with NaOH solution of 12 mol/L [9231 mol/yd³] [21].

Figure 2 presents the weight loss kinetics of prismatic specimens after demolding and throughout their curing (11 days in sealed plastic bags and 14 days dried at 45°C [113°F]). For all batches, a slight loss of mass (less than 0.5% of the initial mass) was observed during specimen's storage in sealed bags. It was followed by a strong loss of mass during drying at 45°C [113°F]. Even if the curve shape differs from one batch to another, final weight loss was mainly depended on the initial water amount of the composition. In fact, the weight lost reached at the end of curing around 7.5% and 8.0% respectively for Na0.12 and Na0.13 compositions, representing lesser than ³/₄ of initial amount of water (Table 2).

Physical and mechanical properties of mortars

Table 4 presents the experimental conditions and mechanical results for all the batches of both compositions. The flexural strength slightly increased when W/S ratio decrease, as in cementitious mortars. However, this difference was not significant comparatively to standard deviation of tests. On the other hand, the compressive strength was widely dispersed: between 10 and 20 MPa [1450 and 2900 psi] for Na0.13 and between 13 and 20 MPa [1885 and 2900 psi] for Na0.12. This dispersion has to be linked firstly to the experimental conditions. When silicon molds were used, the compressive strength was significantly lower than those obtained in metal molds (47% and 35% for Na0.13 and Na0.12 compositions respectively). In fact, the lack of rigidity of the silicon molds led to a distortion of the samples geometric shape. Regarding the laboratory temperature, for Na0.12 composition (i.e. B2 and B3 casted in metal molds), the compressive strength was improved of about 14% when the temperature of laboratory during preparation was 21.5°C [71°F] instead of 18.8°C [66°F]. The decreasing of the soda solution viscosity with temperature [22], explained these improvement. Soda solution with lower viscosity wet better the filler and sand particles and improved the homogeneity of the mortar. A slightly improvement (around 4%) in compressive strength of Na0.12_B3 batch comparatively to Na0.13_B2 batch was observed in accordance with

the lower water content and in spite of the lower sodium hydroxide content (Table 3) and the lower laboratory temperature (21.5 instead of 23.4° C [71 and 74° F], respectively). More test are necessary to confirm this observation.

Despite of dispersion of flexural and compressive strength results, the porosity and the density of different batches (Table 3) of the same composition were very close. Formulation with 0.12 W/S ratio (Na0.12) exhibited a slightly lower porosity and a higher dry density as expected, which could probably compared with the higher compressive strength of this formulation. These results enabled concluding that the high dispersion of compressive strength results and in a lesser extent of flexural strength must not be related to poor repeatability of processes and methods, but mainly to the quality of the molds and the room temperature during casting.

Identification of the reaction products

Figure 3 presents the XRD pattern for Na0.13 and Na0.12 compositions and the identified crystalline phases (at least the three most important peaks for each). The XRD patterns were very similar even if the W/S ratio was different. Crystalline phases present in the mortars, resulting from the alkali-activation of the limestone, were pirssonite (Na₂Ca(CO₃)₂.2H₂O, JCPDS 24-1065) and portlandite (Ca(OH)₂, JCPDS 44-1481). There were also quartz (SiO₂, JCPDS 46-1045) from sand and small amount of calcite (CaCO₃, JCPSD 05-0586) essentially from the unreacted limestone filler. This first result showed that the limestone filler reacted with sodium hydroxide to form a calcium/sodium carbonate hydrate and portlandite following the chemical reaction (3).

 $2NaOH + 2CaCO_3 + 2H_2O \rightarrow Na_2Ca(CO_3)_2 \cdot 2H_2O + Ca(OH)_2$

 $a(OH)_2$ (3)

There was not any significant halo in the background noise of XRD patterns. This allowed excluding any formation of amorphous silicate components resulting from potential alkali-activation of the sand.

Figure 4 shows the average thermal analysis curves of three samples for mortars Na0.12 and Na0.13 and allowed identifying the following dissociation reactions:

- Dehydration of pirssonite at 174°C [345°F], equation (4) Na₂Ca(CO₃)₂.2H₂O → Na₂Ca(CO₃)₂ + 2H₂O (4) - Dehydration of portlandite at 436°C [817°F], equation (5) Ca(OH)₂ → CaO + H₂O (5) - Decarbonation of nyerereite at 777°C [1431°F], equation (6) Na₂Ca(CO₃)₂ → Na₂CO₃ + CaO + CO₂ (6) - Decarbonation of calcite from limestone filler above 800°C [1472°F], equation (7) CaCO₃ → CaO + CO₂ (7)

The dissociation temperatures of pirssonite and nyerereite were consistent with the literature [23]. The thermal analysis curves also presented two crystallographic transformations without mass variation. The first, around 385°C [725°F], corresponded to the transition from low temperature form to the high temperature form of nyerereite [24]. The second, around 568°C [1054°F], was associated with the allotropic transformation of quartz α (from the sand) into quartz β . These results confirmed those obtained by XRD and verified no presence of additional amorphous phase. The weight losses related to the dehydration of pirssonite and portlandite, respectively noted $\Delta m_{pirss(TG)}$ and $\Delta m_{port(TG)}$, were measured on TG curves between 25 and 335°C [77 to 635°F] and between 335 and 560°C [635 to 1040°F] respectively (figure 4).

Quantification of water and reaction products

Firstly, two types of water in the material were distinguished: free or evaporable water $(m_{free w})$ eliminated during drying and bound water $(m_{bound w})$ in pirssonite and portlandite. Secondly, the following assumptions were made:

a) Before demolding, the conservation of molds in sealed bags prevented water evaporation from occurring. In that case, the mass of the specimens at the demolding (3 days) were considered equal to the initial mass of the specimens after casting (m_0). This assumption was very close to reality if we take in account that the specimen's loss of weight during 11 days conservation in sealed plastic bags was very low (< 0.5%, Figure 2).

b) 14 days drying at 45°C [113°F] guaranteed the evaporation of the total free water. So, the relative mass of free water in the specimens (expressed in %) was determined from the following equation.

 $\Delta m_{\text{free w}} = 100 \frac{m_0 - m_{28d}}{m_0} \tag{8}$

where m_{28d} was the mass of the specimens at the end of the drying (at 28 days). This mass included only the mass of the bound water ($m_{bound w}$) and the mass of initial solid material (m_{solid}) (i.e. limestone, sand and solid sodium hydroxide (equation (9)):

 $m_{28d} = m_{bound w} + m_{solid}$

(9)

c) Crushing of samples for DTA-TGA testing did not modify the composition of the mortars particularly concerning the pirssonite amount. However, as will be discussed here after, it was possible that portlandite procured from alkali-activation reaction were partially carbonated during curing, crushing and conservation until DTA-TGA tests.

The relative weight loss (in %), corresponding to the dehydration of pirssonite and portlandite, measured by TGA ($\Delta m_{pirss w (TGA)}$ and $\Delta m_{portl w (TGA)}$), was linked with the previous masses by the equations (10) and (11).

$$\Delta m_{\text{pirss w (TGA)}} = 100 \frac{m_{\text{pirss w (TGA)}}}{m_{\text{bound w}} + m_{\text{solid}}}$$
(10)
Arra = 100 m_{\text{portl w (TGA)}} (11)

$$\Delta m_{\text{portl w}(\text{TGA})} = 100 \frac{100}{m_{\text{bound w}} + m_{\text{solid}}}$$
(11)

where: $m_{pirss w (TGA)}$ and $m_{portl w (TGA)}$ were respectively the mass of bound water of pirssonite and portandite in the dry sample tested and consequently (equation (12)).

$$m_{pirss w (TGA)} + m_{portl w (TGA)} = m_{bound w}$$

(12)

From the previous quantities, the relative amount of pirssonite and portlandite in the specimens with respect to their initial mass, before drying (m_0) , were determined according the following equations:

$$\Delta m_{\text{pirss (TGA)}} = \Delta m_{\text{pirss w (TGA)}} x \frac{M_{\text{pirss}}}{2.M_{\text{water}}} x \frac{100 - \Delta m_{\text{free w}}}{100}$$
(13)

$$\Delta m_{\text{max}} = \Delta m_{\text{max}} y \frac{M_{\text{portl}}}{100 - \Delta m_{\text{free w}}}$$
(14)

 $\Delta m_{\text{portl (TGA)}} = \Delta m_{\text{portl w (TGA)}} x \frac{M_{\text{portl}}}{M_{\text{water}}} x \frac{100 \text{ Jm}_{\text{ree w}}}{100}$ (14) where M_{pirss} , M_{portl} and M_{water} were respectively molar weight of pirssonite (242g/mol [53x10⁻² lb/mol]), portlandite (74g/mol [16x10⁻² lb/mol]) and water (18g/mol [40x10⁻³ lb/mol]).

On the other hand, it was possible to determine also the relative amount of portlandite (equation (15)) in the specimens indirectly, using the previous relative amount of pirssonite $(\Delta m_{\text{pirss (TGA)}})$ and the stoichiometric amount of both products from equation (3).

$$\Delta m_{\text{portl (pirss)}} = \Delta m_{\text{pirss (TGA)}} x \frac{M_{\text{portl}}}{M_{\text{pirss}}}$$
(15)

This value does not take in account the probable carbonation of portlandite during curing and crushing of the specimens and were compared to the previous value $\Delta m_{\text{portl}(TGA)}$ determined directly from DTA-TGA tests to determine the carbonation degree.

The Table 5 presents the analytical results of all the previous determined quantities for each one prismatic specimen tested and for the five batches. The following comments were done:

- a) All the specimens of each batch presented very close values for all determined quantities ensuring the homogeneity of each batch and the reliability of employed methods.
- b) All the batches of each formulation presented also very close values ensuring the good repeatability of the employed processes and testing conditions.
- c) The formulation Na0.13 with higher content of soda solution produced more pirssonite and more portlandite than the Na0.12 formulation, in accordance with calorimetric measurements.
- d) The relative amount of portlandite determined directly by DTA-TGA tests ($\Delta m_{pirss (TGA)}$) was about 20-25% lower than that determined indirectly by pirssonite ($\Delta m_{portl (pirss)}$).

Quantification of remaining reagent

Based on the relative amount of pirssonite $(\Delta m_{pirss (TGA)})$, it was possible determining the remaining relative amounts of sodium hydroxide $(\Delta m_{r NaOH})$ and calcareous filler $(\Delta m_{r CaCO3})$ according the following equations.

$$\Delta m_{r NaOH} = \Delta m_{NaOH} - (\Delta m_{pirss (TGA)} x \frac{2M_{NaOH}}{M_{pirss}})$$
(16)
$$\Delta m_{r CaCO3} = \Delta m_{CaCO3} - (\Delta m_{pirss (TGA)} x \frac{2M_{CaCO3}}{M_{pirss}})$$
(17)

 Δm_{NaOH} and Δm_{CaCO3} were the initial relative quantities solid sodium hydroxide and limestone filler used for the mortar preparation (presented in Table 3), M_{CaCO_3} and M_{NaOH} were respectively the molar weight of limestone (100g/mol [22x10⁻² lb/mol]) and sodium hydroxide (40g/mol [88x10⁻³ lb/mol]). Table 6 presents the composition for all alkali-activated specimens. Whatever the W/S ratio and the experiments conditions, the composition balance after alkali-activation was very close to 100% ensuring the coherence and reproducibility of the methodology proposed to determine free water, new products and remaining reagents. When the W/S ratio increased, pirssonite and portlandite quantities also increased (from 19% to 21.5% for pirssonite and from 5.8% to 6.5% for portlandite) and the remaining limestone filler decreased: (from 5.0% to 2.5%). These increases in reaction products and the decrease in the remaining limestone were explained by the increase of the sodium hydroxide amount between the Na0.12 and Na0.13 formulations. The higher strength of Na0.12 composition could only be explained from slightly lower porosity, higher density and consequently to a more efficient microstructure arrangement. This point should be verified by Secondary Electron Microscope (SEM) observations.

CONCLUSIONS

This study presents a new type of binder obtained by activation of calcareous filler by sodium hydroxide. The investigation on the kinetics reaction, physical properties (i.e. strengths, porosity and density), the identification and quantification of reaction products, for two compositions allows the following conclusions:

a) Highly concentrated sodium hydroxide solution dissolves limestone filler in few minutes and forms progressively crystallized sodium/calcium carbonate hydrate (pirssonite) and calcium hydroxide (portlandite) in mortars with siliceous sand without formation of any amorphous phase.

b) This reaction leads to setting and hardening of mortar and reach according experimental conditions between 17 and 20 MPa [2500 and 2900 psi] as compressive strength and 3 and 4 MPa [500 and 600 psi] as flexural strength after 14 days wet plus 14 days dry curing.

c) The higher mechanical strength is obtained on binders prepared with the smallest water to solid ratio at a laboratory temperature upper than 20°C [68°F].

d) The quantities of reaction products and remaining reagents are determined by weight loss measures and thermogravimetric analyses data with a higher reliability. They corroborated the initial composition of mortars.

e) The amounts of pirssonite and portlandite formed by alkali-activation of limestone filler correspond with the complete reaction of sodium hydroxide content in the mortar.

The previous results open interesting possibilities to improve the performances of these new type materials based on alkali-activated calcareous filler.

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