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Mechanical and thermal modification of mordenite-rich tuff and its effect on cement pastes

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Abstract
To overcome performance deficiencies of the raw mordenite-rich tuff in the partial replacement of Portland cement in cement paste, the material was subjected to different treatments: calcination at 300 °C and 500 °C, grinding to very high specific surface areas, co-grinding with Portland cement, and separate or co-grinding with granulate blast furnace slag. The resulting materials were examined by tracking changes in density, particle shapes, and size distributions. The blended cement pastes were examined by monitoring the water demand, setting time, hydration process by isothermal microcalorimetry, degree of hydration, non-evaporable water content and free $Ca(OH)_2$ by TGA-DSC analysis. The findings provide clear evidence that with the activation techniques, the performance of the raw mordenite-rich tuff is improved.

Keywords: mordenite-rich tuff, treatment techniques, calcination, grinding

1. Introduction
Many natural materials are currently used as pozzolanic agents aimed at improving the quality of cement-based materials. Natural zeolites are among the most common and promising minerals for many civil, environmental, and chemical applications. Despite their distinct crystalline structure, their pozzolanic activity is almost as high as that of amorphous mineral additives [1]. Therefore, they could be used as an alternative to artificial pozzolanic material to replace parts of Portland cement. Their use as natural pozzolans has increased markedly [1,2] because of their abundance, low extraction and processing costs, large and diverse deposits, low environmental impact, and remarkable physical and chemical properties [3]. Despite these obvious advantages, the properties of zeolites vary greatly between species [4]. Mordenite, heulandite, and clinoptilolite are the most common natural zeolites on earth; the last two have the same crystalline structure and are the most widely used as natural pozzolans, while mordenite is used in smaller quantities [5,6]. In addition, there is limited information about the properties and hydration characteristics of blended cements incorporating mordenite. Some studies have looked into the use of mordenite as a supplementary cementitious material (SCM) to see how it performs in cement-based systems and its pozzolanic behaviour. It was revealed that mortars made with partial replacement of cement with mordenite showed a delay in initial and final setting times, greater consistency, lower fluidity, and lower density [7]. The pozzolanic reaction between mordenite zeolite and the hydration products of cement is enhanced by the mordenite content in the samples and depends on the Si/Al ratio and the surface area [8]. Other researchers found that tuffs rich in mordenite must be calcined at 760 for 12 h to achieve optimal pozzolanicity [9]. The pozzolanic activity of natural mordenite-type zeolite was determined during a reaction with a saturated lime solution at 40 °C. However, the pozzolanic reaction is not responsible for all the Ca^{2+} consumed in solution; zeolite transformation from mordenite to clinoptilolite has been observed [10]. Higher specific surface areas yield higher short-term

pozzolanic activity when portlandite is consumed by mixing lime with mordenite tuffs ground to different grain sizes [11].

Willing to contribute to a state of the art knowledge about the basic mechanisms related to mordenite-rich tuff effects on cementitious materials, we have investigated, in a previous research [12], the benefits of its use as a partial replacement (up to 20%) of Portland cement, from the physico─mechanical and microstructural point of view. The first stage of this study focused on the pastes, including water requirement, setting time, hydration heat and free $Ca(OH)_2$ content.

It was found that mixtures containing mordenite-rich tuff had the potential to replace Portland cement by up to 20%. Incorporation of the mordenite-rich tuff increased the hydration heat up to 7 h and accelerated the appearance of the maximum thermal effect by allowing the C_3A to undergo renewed rapid hydration and convert the ettringite to monosulfoaluminate. The water demand of mordenite-rich tuff-blended cement pastes rose as the tuff content increased due to the micropores inherent in its structure. The addition of the mordenite-rich tuff slowed the initial setting time while speeding up the final setting time. The free $Ca(OH)_2$ levels in cement pastes containing up to 20% mordenite-rich tuff are 7.5%, 9%, and 21% lower than in control paste at 7, 28, and 90 days, respectively. Because portlandite is a reactive compound that can cause durability issues, the measured free $Ca(OH)_2$ content in the blended cement pastes must be further reduced. As a result, the reactivity of mordenite-rich tuff with lime was termed insufficient. The use of mordenite-rich tuff in its natural state is not always as effective as it could be. Then, the improvement of its reactivity could possibly overcome this shortcoming. According to the researchers, the most successful treatments are calcination, milling, and chemical activation [13–16].

Research has been done to improve pozzolanic activity by subjecting the natural zeolite to calcination or milling pre-treatments [17–19]. However, little is known about the mechanical and thermal activations of mordenite-rich tuff and their impact on cement-based material properties [20].

Milling reduces particle size distributions, increasing specific surface area and reaction speed, but the crystalline structure of natural zeolite is unaffected. Three approaches were used to extend the limits of conventional milling: milling the material to very high specific surface areas to make it as reactive as possible; separate or co-grinding the material with GGBFS; as well as its co-grinding with Portland cement.

A calcination pre-treatment alternative has been used to increase mordenite-rich tuff pozzolanic activity.. The objective of the calcination pre-treatment was to improve the physical properties and break the crystalline structure of the material to allow it to react faster or more efficiently as a pozzolan, resulting in an improved performance in cementitious systems.

The purpose of this study was to assess the behaviour of mordenite-rich tuff as a supplementary cementitious material as well as the performance of this raw natural pozzolan versus pre-treated mordenite-rich tuff by calcination or milling, with substitution percentages of 5–10–15–20% in ordinary Portland cement. Variable milling parameters and calcination temperatures are used to achieve this. The treated tuffs were compared to the raw mordenite-rich tuff in terms of density, specific surface area, particle size and shape, water requirement, setting time, hydration process, $Ca(OH)_2$ content, non-evaporable water content, and degree of hydration to show how the activation techniques perform on the tuff powder and pastes.

Experimental techniques including isothermal microcalorimetry, thermogravimetric (TGA) coupled with differential scanning calorimetry (DSC), and scanning electron microscopy (SEM) were implemented. Using these techniques yielded new information on the effects of raw and pre-treated mordenite-rich tuff on PC hydration and $Ca(OH)_2$ consumption, as well as a better understanding of the fresh and hardened performance of the paste samples.

2. Presentation of activation techniques

2.1.Thermal activation

In the thermal treatment by calcination, the heating time and the type of cooling are the parameters of great importance in the activation of a pozzolan. The optimum calcination temperature corresponds to the temperature at which the pozzolan minerals crystallize without being followed by recrystallization. The stability of the crystal plays an essential role in the solubility. This is the reason why, in a metastable state, calcined pozzolans are more reactive than in a natural, more stable state [21]. In addition, cooling has a great influence on the stability of minerals; to reach better reactivity, the cooling must be rapid enough to freeze the minerals in their metastable states acquired at the optimum calcination temperature. Notwithstanding the importance of these parameters, the literature does not record any standard calcination test setting other than the heating and cooling methods.

Calcination procedure

The raw mordenite-rich tuff powder defined in the previous research [12] was calcined in a Nabertherm type P330 programmer furnace at 300 °C or 500 °C. In porcelain crucibles measuring 6 cm in high and 4 cm in diameter, 30 grams of tuff were heated at a heating rate of 10 °C/min to reach the desired temperature; this temperature was then kept constant for 5 hours. At the end of this period, the calcined tuffs were quickly transferred into a desiccator and cooled at ambient temperature (20 °C).

2.2.Mechanical activation

Using the pozzolan reactivity's improvement method, mechanical activation, traditionally achieved by grinding grains to a higher specific surface area, proved to be an easy, practical, and efficient technique.

The objective of this technique is to improve the properties of mordenite-rich tuff in order to enhance its ability to react faster or more efficiently. This will result in better performance in cement systems.

In order to improve the impact of the mechanical activation, which aims to increase the fineness of the material by grinding, the following research intends to grind the tuff separately or by co-grinding with granulate blast furnace slag (GGBFS), as well as co-grinding with Portland cement. The device used to reach this objective was a vibratory disc mill RS 200.

3. Analysis of treated tuff powders

3.1. Calcined tuff

The raw mordenite-rich tuff powder (TB) had a density of 2.29 kg/m^3 and a specific surface area of 460 m^2/kg. T300 and T500 were assigned to the tuffs after calcination at 300 °C and 500 °C, respectively. The T300 had a lower density (2.254 kg/m^3) and a higher specific surface area, 541 m^2/kg, compared to TB particles. On the other hand, the reduction in surface area of T500 was coupled with a decrease in density (337 m^2/kg and 1.945 kg/m^3). Calcination results in an agglomeration of particles up until temperatures of 800 °C, when sintering of the zeolite particles occurs [22–24]. The decrease in the specific surface area of zeolites after calcination is due to a decrease in the microporosity on the crystal surfaces of zeolites, which is caused by slight crystal structure decompositions [15,25].

The particle size curves and the SEM micrographs of the two tuffs compared to that of the TB are shown in Fig.1 and Fig. 2, respectively.

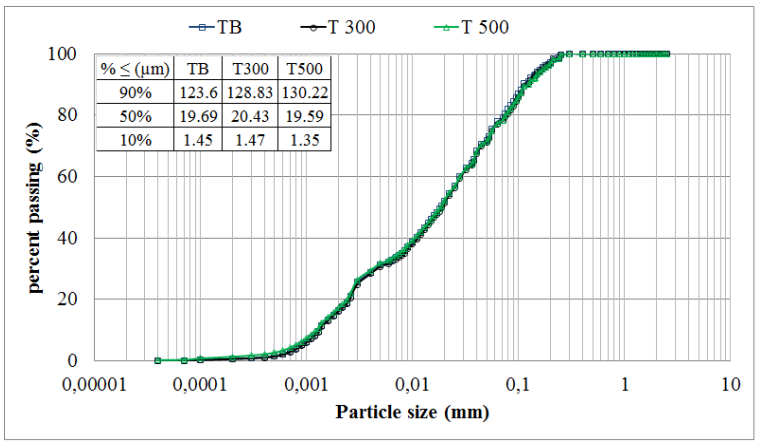


Fig. Erreur ! Il n'y a pas de texte répondant à ce style dans ce document.**1.** Particle size distribution curves of T300 and T500 powders

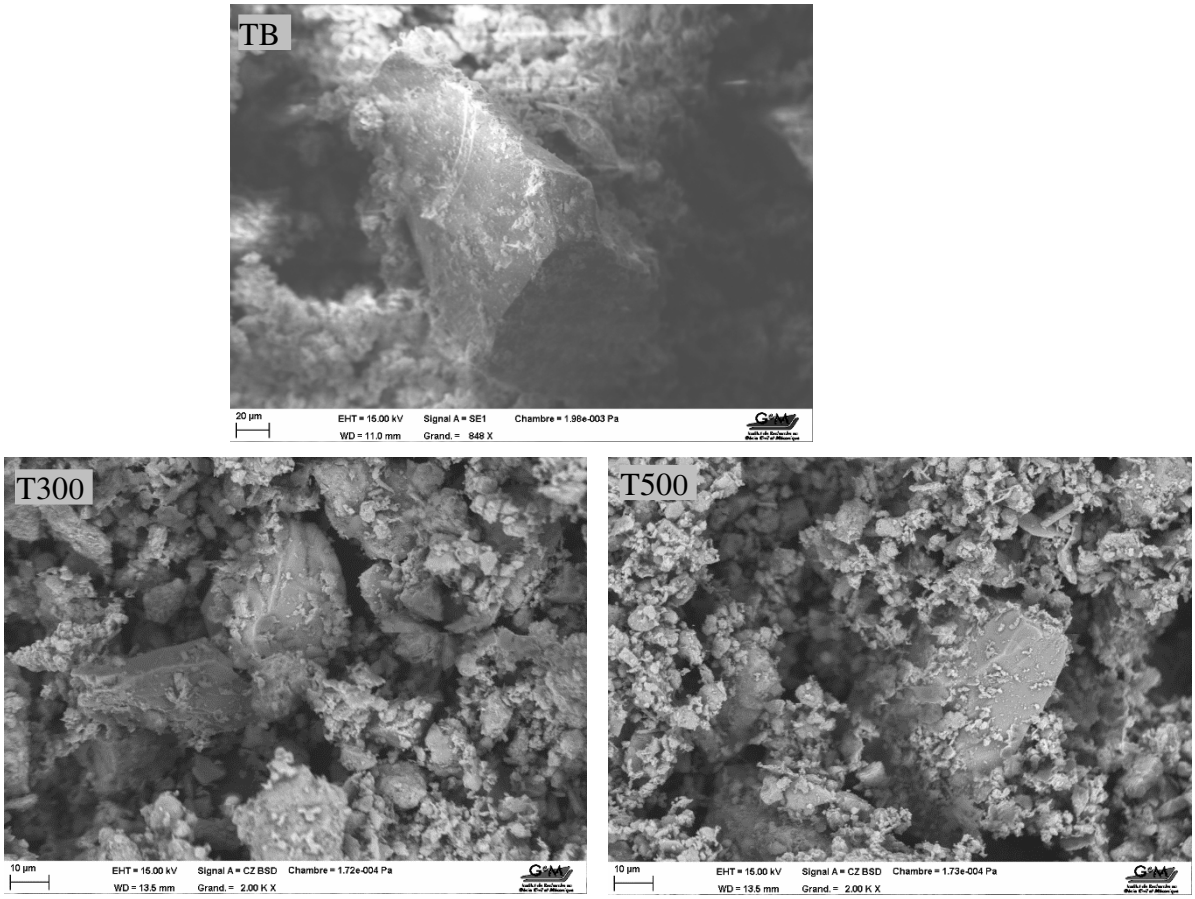


Fig. 2. SEM micrograph of the raw and calcined tuff

Fig. 1 illustrates that calcination has been associated with a slight increase in the particle size, which is probably due to the agglomeration of particles by sintering at high temperatures [23,26,27]. This effect is qualitatively confirmed in the SEM images shown in Fig. 2. From the images in Fig. 2, it is demonstrated that calcination resulted in an agglomeration of particles, with many of the finer particles becoming adhered to the surfaces of larger particles.

3.2.Grinded tuff

3.2.1. Grinding to high specific surface area

The raw mordenite-rich tuff (TB) powder with a density of 2.29 kg/m^3 and a specific surface area of 460 m^2/kg was subjected to fine grinding for 14 min and 18 min to reach a specific surface area of 670 and 860 m^2/kg, respectively. It is noticed that the density is not affected by the grinding operation.

The size and shape of the ground tuffs (T670 and T860) were measured by laser scattering and scanning electron microscopy (SEM) respectively, and results are shown in Fig. 3 and Fig. 4.

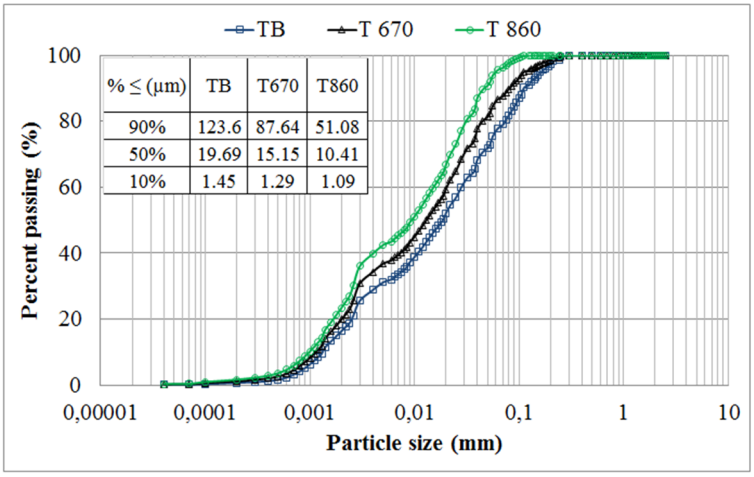


Fig. 3. Particle size distribution curves of T670 and T860 powders

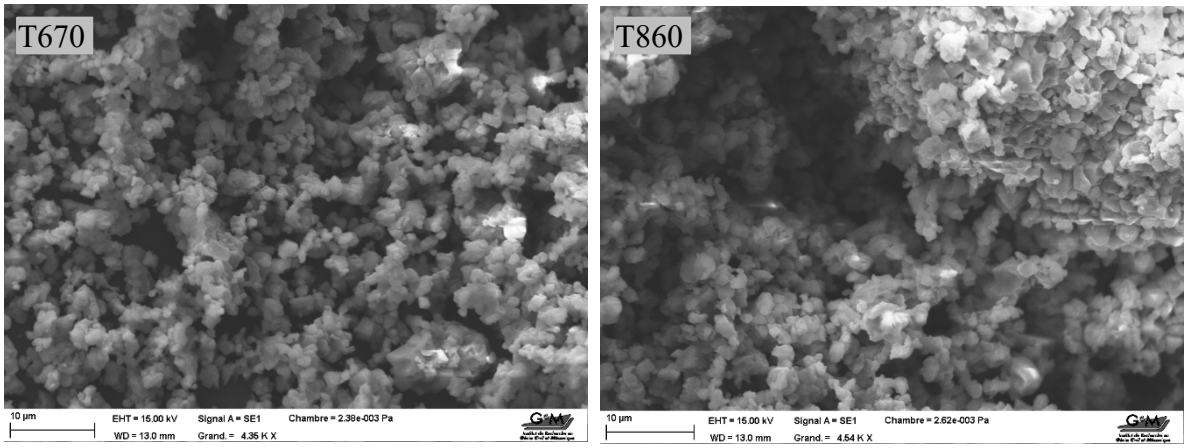


Fig. 4. SEM micrograph of T670 and T860

The particle size gradually decreases as the specific surface area increases. The prolonged grinding operation completely eliminated fractions greater than 100 µm and increased the percentage of the fine fractions.

The SEM micrographs in Fig. 4 indicate that the particles of the tuff after prolonged grinding to high specific surface areas are less agglomerated than in the raw tuff (TB). After grinding, the irregular shape of the particles is transformed into spherical and elliptical ones.

3.2.2. Grinding with GGBFS

The raw mordenite-rich tuff powder (TB) was replaced by 30% (by mass of TB) of GGBFS and underwent two types of grinding. This level was achieved by preliminary tests on the degree of pozzolanicity of the mixture by measuring the amount of free Portlandite in the mixtures.

Separate grinding (BIL)

The tuff received in bulk form was crushed and then grounded for 4 min until a specific surface area of 460 m^2/kg was obtained, with a density of 2.29 kg/m^3. GGBFS with a density of 2.88 kg/m^3 and a specific surface area of 405 m^2/kg was then mixed with the grounded tuff. After homogenisation, the powder thus obtained, named BIL, had a density of 2.47 kg/m^3 and a specific surface area of 444 m^2/kg.

Co-grinding with GGBFS (CBL)

The tuff received in bulk form was crushed and then co-grinded with GGBFS for 3 min to reach a specific surface area of 434 m^2/kg. The density of the powder obtained was 2.51 kg/m^3.

The size and shape of the BIL and CBL are shown in Fig. 5 and Fig. 6, respectively.

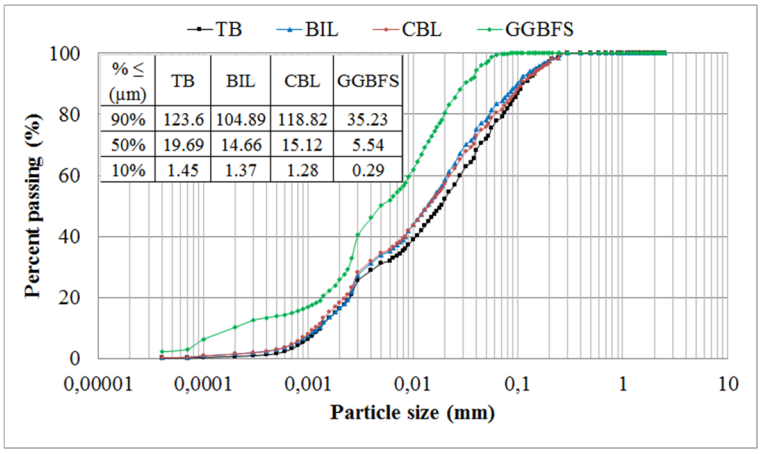


Fig. 5. Particle size distribution curves of BIL and CBL

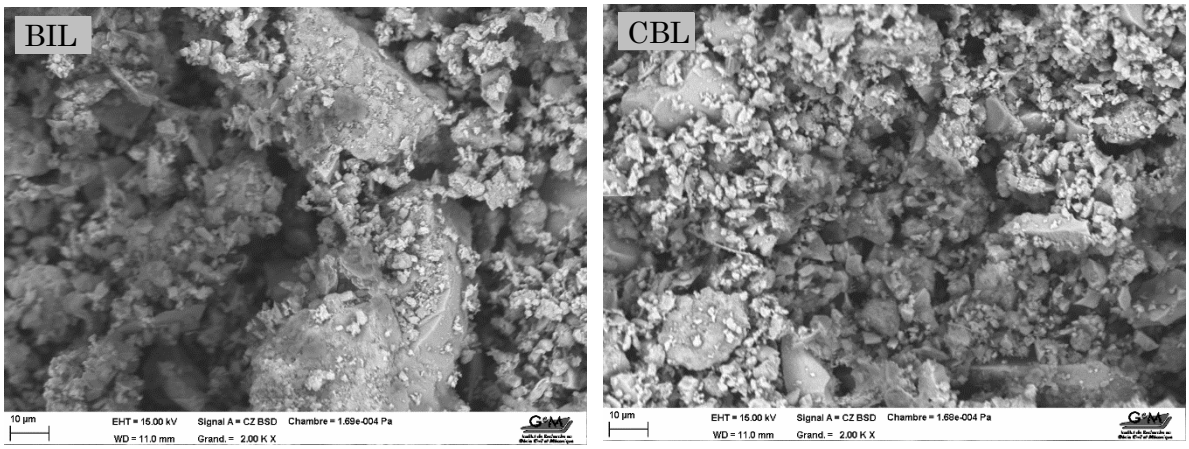


Fig. 6. SEM micrographs of BIL and CBL

The SEM micrographs indicate that the BIL and CBL particles have an irregular shape.

From the particle size distribution shown in Fig. 5, it can be seen that the incorporation of GGBFS into the initial tuff powder reduces the amount of coarse particles. In fact, 90% of them are less than 104.89 µm and 118.82 µm in the BIL and CBL powders, respectively.

3.2.3. Co-grinding with Portland cement (CBC)

The cement CEMI 52.5/R was partially replaced by 5, 10, 15, and 20% of crushed mordenite-rich tuff (TB) and then grinded for 20min, 18min, 18min, and 15min, respectively to reach a specific surface area of around 600 m^2/kg. The densities and specific surface areas of the

powders (cement+% tuff) thus obtained are listed in Table 1. The particle size distribution of tuff co-grinded with cement is shown in Fig. 7. The SEM morphologies are represented in Fig. 8.

Table Erreur ! Il n'y a pas de texte répondant à ce style dans ce document.**1**: densities and specific surface areas of tuff co-grinded with Portland cement

Material	PC	TB	5 CBC	10 CBC	15 CBC	20 CBC
Density	3.14	2.29	3.04	3.02	2.87	2.79
Specific surface area (m^2/kg)	440	460	663	613	634	632

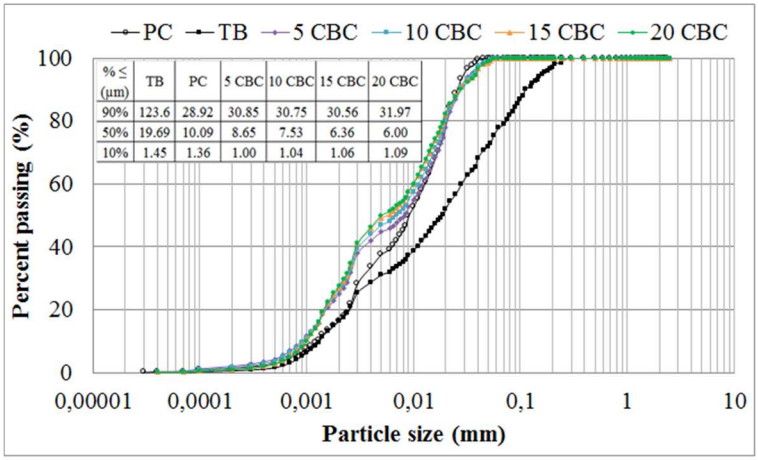


Fig. Erreur ! Il n'y a pas de texte répondant à ce style dans ce document.**7.** Particle size distribution curves of tuff co-grinded with Portland cement

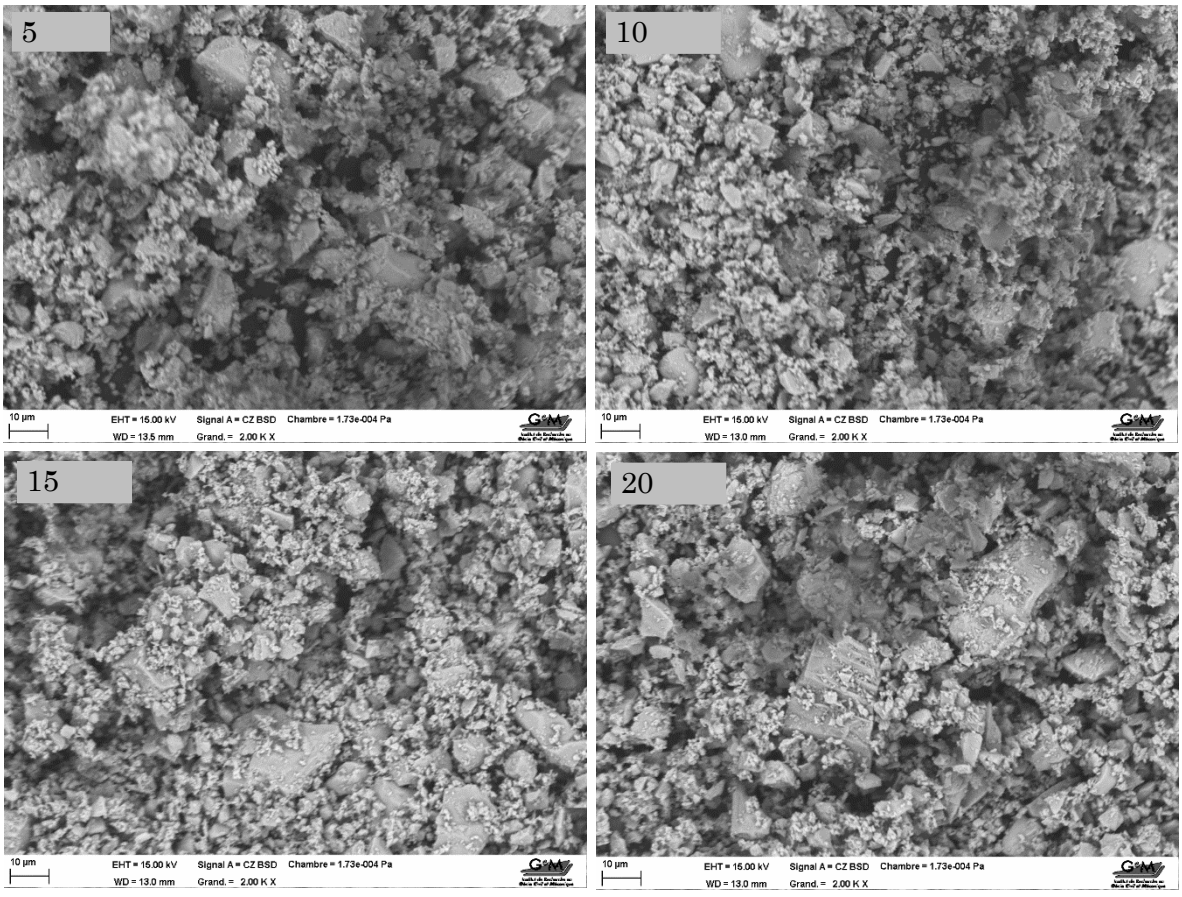


Fig. 8. SEM micrographs of tuff co-grinded with Portland cement

From the particle size distribution shown in Fig.7, it can be seen that the mean diameter of the particles decreases as the amount of tuff co-grinded with Portland cement increases. The cements resulting from the co-grinding of tuff with cement are slightly finer than Portland cement CEM I 52.5 (PC).

Fig. 8 shows that the particles of the powders containing different levels of tuff co-grinded with PC had an irregular shape. Moreover, other angular-shaped particles with a rough surface texture relating to PC grains are also observed [28].

4. Formulation of cement pastes, cure condition and test methods

To formulate the cement pastes, five substitution rates (by mass) of PC by tuff have been adopted, including 0, 5, 10, 15, and 20%. Except for GGBFS-incorporating tuff, only one substitution rate has been studied: 10% of cement was replaced with GGBFS (paste 10L) or GGBFS-incorporating tuff (pastes BIL and CBL). 24 cement pastes with a water/binder ratio (w/b) of 0.35 are prepared and mixed according to NF EN 196-1 [29]. The sample curing conditions have been described in previous research [12].

The test methods aim to study the influence of the substitution rate and the method of activation of the mordenite-rich tuff on the performance of the cement paste. The experimental campaign includes the normal consistency water requirement, the setting time, monitoring the evolution of the hydration process (heat and kinetics of hydration), the free $Ca(OH)_2$ content, the non-evaporable water and the degree of hydration. The experimental procedure used is that adopted in [12].

5. Results and discussions

5.1. Water demand and setting time

The physical properties of fresh cement pastes are listed in Table 2.

Table 2: physical properties of fresh cement pastes

Pastes	Water demand (%m/m)	Initial setting time (min)	Final setting time (min)
100 PC	30.5	59	414
5 TB	32	63	359
10 TB	32.5	65	339
15 TB	34	65	305
20 TB	35	72	279
5 T300	32.5	67	278
10 T300	33.5	78	274
15 T300	34.0	79	274
20 T300	35.5	91	271
5 T500	32.0	66	279
10 T500	33.0	68	294
15 T500	33.5	74	294
20 T500	35.0	90	339
5 T670	33.0	74	258
10 T670	34.5	90	269
15 T670	36.0	86	327
20 T670	37.5	90	331
5 T860	33.0	64	240
10 T860	34.0	63	254

15 T860	35.5	72	309
20 T860	36.0	74	321
5 CBC	32.0	46	309
10 CBC	33.5	60	330
15 CBC	35.0	58	330
20 CBC	36.0	75	363
BIL	32.0	59	294
CBL	31.0	55	319
10L	30.5	56	339

Water demand

It can be seen from Table 2 that the tuff treatment techniques cause an increase in the required water percentage proportional to the tuff admixing ratio.

The increase in the water demand may be due to the reduction of the base binder (cement) in the mixture as the tuff content increases. Increasing the overall volume of the binder as the tuff content increases requires more water to form a paste of the same standard consistency as the control paste (100 PC) [5].

Calcination of the raw tuff (TB) at 300 °C affected slightly the workability of the mixture; in which the water requirement is only increased by less than 3% compared to mixtures containing the untreated tuff. Calcination at 500 °C had no effect on water demand compared to that required in TB pastes. The decrease in water requirement after calcination at 500 °C could be associated with the decrease in specific surface area of T500 compared to T300 [30]. As reported in the literature, calcination of natural zeolites was shown to improve the workability of their pastes through destabilization of the zeolite crystalline structure. In addition, agglomeration of the zeolite particles and the dehyroxylation of the clay impurities during calcination, might also have contributed to the improvement of the workability of the natural zeolite mixtures [15].

The specific surface area of T500 decreased by 26.74% compared to that of TB. However, the specific surface of T300 increased by 17.61%. These results demonstrate that calcination at 500 °C can reduce the water requirements of the tuff and eliminate the unwanted high water demand. A similar result is reported by previous research [17], which observed that the calcination of a zeolite at different temperatures can reduce or keep the water requirement constant.

When heated, pozzolans undergo chemical and structural changes that exhibit two antagonistic effects. The positive effects cover the loss of water in the glassy or zeolite phases and the destruction of the crystal structure. While the negative effect is evidenced by the decrease in specific surface area, devitrification and crystallization [31].

Mixtures containing different levels of T670 and T860 show a fairly high water demand, which increases with increasing the content of tuff in the mixtures. This increase is around 7% and 6% in 20 T670 and 20 T860, respectively. The high specific surface area and the porous structure of the zeolite increase the water demand in proportion to the dosage of the zeolite [8,32].

Although there is no linear or direct relationship between the specific surface area and the water requirement of tuff, the specific surface area can be referred to as a major parameter explaining the effect of grinding on water requirement. Moreover, although the specific surface area of tuff co-grinded with Portland cement exceeds 600 m^2/kg; the need for water increased only slightly (< 3%).

Unlike the other blends, those of BIL, CBL, and 10L showed a decrease of 1.54%, 4.62%, and 6.15% in water demand of 10 TB, respectively. Adding GGBFS to the tuff increased the fictitious ratio of w/b (visual implication). This is the dilution effect of the mixture. Mixtures containing GGBFS are generally more workable and much easier to set up [33].

Setting time

In general, as the replacement levels of the tuff increased, there was a greater delay in setting times. The replacement of the cement at a level of 20% resulted in the greatest delay in the initial setting time, which reached 15 min in the case of the T860 and CBC pastes and 30 min in the case of the T300, T500, and T670 pastes.

Whereas the final setting time is prolonged and tends to converge towards that of the control paste as the tuff content increases. In fact, a 20% mass replacement of Portland cement with tuff resulted in an acceleration of the final setting time by 51 min, 75 min, 83 min, 94 min, and 143 min in the case of CBC, T500, T670, T860, and T300 pastes, respectively.

In comparison with the TB pastes, calcination induces an extension of the initial setting time of about 19 min at a 20% mass replacement of Portland cement. Grinding to a specific surface area of 670 m^2/kg has also delayed the initial setting by 25 min, whereas the effect of grinding to a specific surface area of 860 m^2/kg was not significant.

Compared to the control cement paste and 10TB paste, the inclusion of GGBFS did not show a significant effect in the initial setting but accelerated the final setting. Furthermore, when the level of replacing cement by GGBFS was only 10% and no superplasticizers were incorporated in the paste formulation, the hydration was not retarded. The adsorption of superplasticizers over the surface of cement particles and the lower cement content (dilution effect) can retard the coagulation establishing contacts between particles and the formation of hydrates [34].

The final setting times of the pastes resulting from the different activation techniques are significantly less than that of the control paste.

In comparison with TB pastes, the replacement of Portland cement by 5 to 15% of calcined tuff significantly accelerates the final setting time. When the tuff was calcined at 300 °C, the final setting time was accelerated by 81 min, 65 min, and 31 min compared to 5 TB, 10 TB, and 15 TB, respectively. Calcination at 500 °C accelerated the final setting time by 80 min, 45 min, and 11 min, respectively, when compared to 5 TB, 10 TB, and 15 TB. However, the 20 T500 paste prolonged the final setting by 60 min compared to 20 TB.

Due to the decrease in the specific surface area of the tuff after calcination at 500 °C, the diffusion of water becomes slower, which leads to a slowing down of the reaction of C_3A, and consequently the rate of crystallization of CSH is slowed down and the setting time is extended [35].

Prolonged grinding of the tuff had two opposite effects on the final setting. These effects are related to the tuff content in the pastes. Indeed, the pastes containing 5 and 10% of grinded tuff showed a shorter final setting time than those of TB pastes. The fastest final setting was shown in the cases of 5 T860 and 10 T860 by 119 min, and 85 min, respectively, whereas 15 and 20% content delayed this time.

The slowest final setting was observed in the 15 T670 and 20 T670 pastes, which occurred 22 min and 52 min after that of 15 TB and 20 TB, respectively.

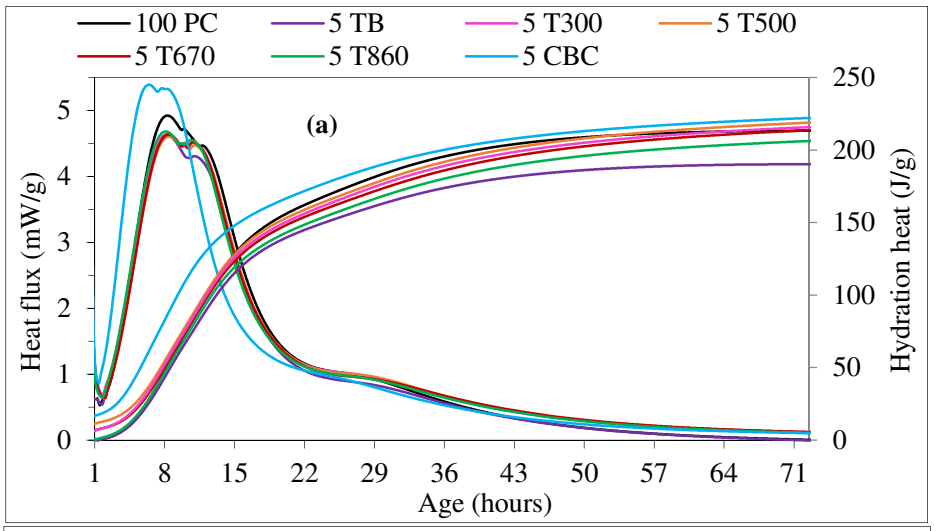
Co-grinding the tuff with Portland cement accelerated the final setting when the content of the tuff was less than 15%. The faster final setting was shown in the case of the 5 CBC paste, which was observed 50 min prior to the 5 TB paste. While in the case of 15 CBC and 20 CBC pastes, this time was delayed by 25 min and 84 min, respectively.

The results showed that fine binders (T670, T860 and CBC) had a shorter initial and/or final setting time for 5% and 10% tuff content regardless of the grinding method (co-grinding or separate grinding). Similar results related to the setting time of fine mixtures have been reported by previous researchers [32,36].

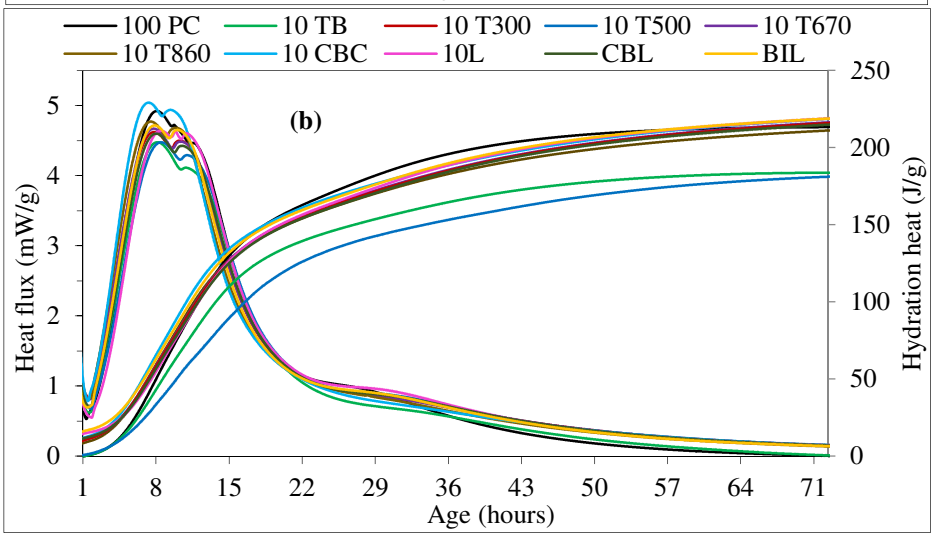
The standard specifications of EN 197-1 limits the initial setting time to a minimum of 45 min. As seen from Table 2, all cement pastes meet these requirements [37].

4.2. Monitoring the hydration process by isothermal microcalorimetry

Fig. 9 (a-d) shows the rate of heat generation and total heat released as a result of cement hydration obtained from an isothermal calorimetry test at 20 °C.


100 PC
5 TB
5 T300
5 T500
5 T670
5 T860
5 CBC
(a)
Heat flux (mW/g)
Hydration heat (J/g)
Age (hours)

392


100 PC
10 TB
10 T300
10 T500
10 T670
10 T860
10 CBC
10L
CBL
BIL
(b)
Heat flux (mW/g)
Hydration heat (J/g)
Age (hours)

393

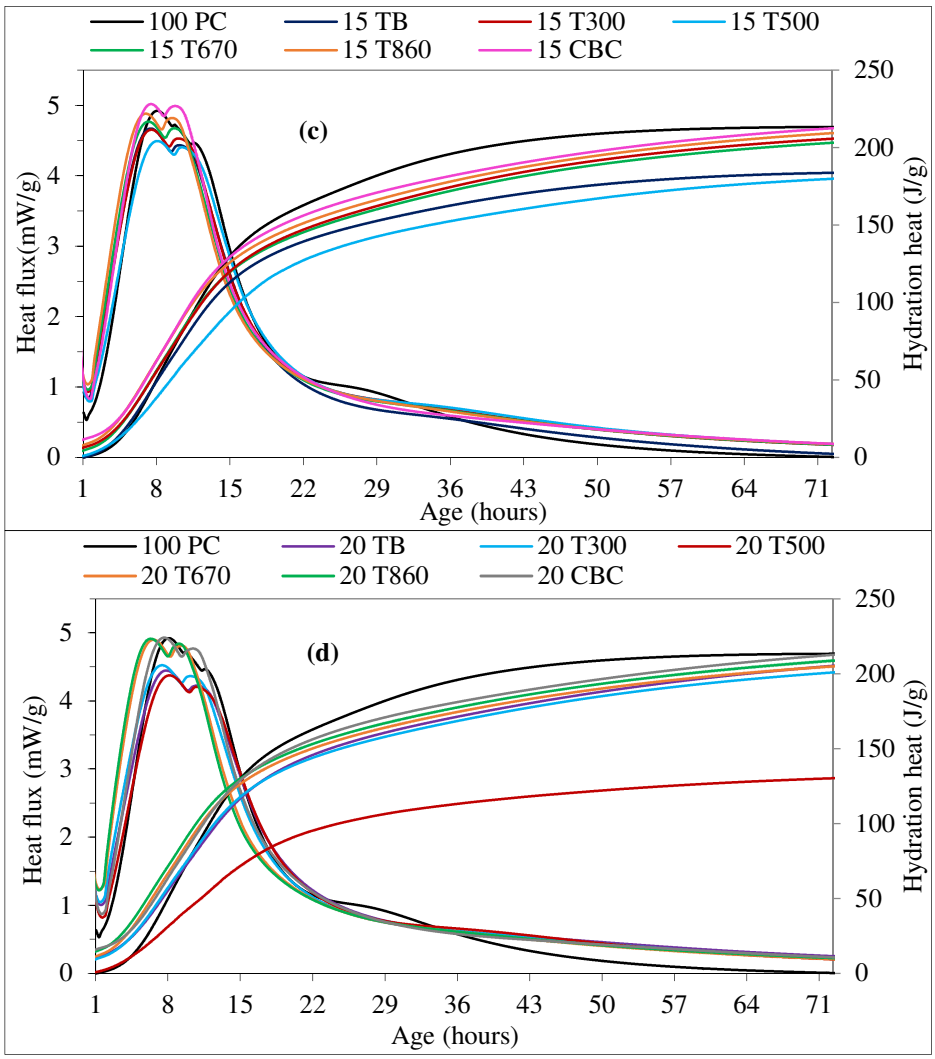


Fig. Erreur ! Il n'y a pas de texte répondant à ce style dans ce document.**9.** Heat flux and hydration heat of the pastes containing the treated tuffs

By performing an overarching analysis of the rate of heat generation curves, it can be seen that, except for the pastes containing the T670 and T860 tuff, the intensity of the maximum peak decreases as the content of treated tuff increases. Overall, the tuff may have hindered the total extent of cement hydration [13].

Generally, the pastes containing pozzolans have reduced the heat of hydration compared to Portland cement during the first hours of the test [38,39]. Replacing cement with zeolite results in less heat of hydration without a significant reduction in setting time [8].

The baseline of heat evolution during the induction period increased as the tuff content increased. Therefore, the development of hydration heat is faster in the initial hydration phase. The addition of the tuff advances the onset of the acceleration period and greatly accelerates the C_3S hydration rate at early stages [40].

All treated tuff pastes show a shortened deceleration period and an onset time of the heat flux peak corresponding to the transformation of trisolfoalumite to monosulfate. This further highlights the accelerating effect of the hydration process by the tuff treated by the different techniques [41].

At 72 h, the heat flux of the pastes containing the treated tuff is much greater than that of 100% PC, in particular for the substitution rates of 15% and 20%. This highlights the fact that the activation techniques fully incorporated the tuff in the cement hydration reaction [13].

A more detailed assessment of the effect of tuff treatment on the hydration of blended systems is shown in Table 3. This table shows the overall experimental heat of hydration released over a period of 72 hours (exper hydr heat) and the hydration heat calculated for pure cement (calc hydr heat). The calculated heat of hydration was calculated according to the following expression:

$$Q_{\text{calc hydr heat}} = \frac{Q_{\text{exper hydr heat}}}{100 - \%\ \text{substitution}} \times 100 \quad (1)$$

Table 3: Characteristics of the heat flux peak (q_{max}) and the total hydration heat of the different pastes

Pastes	Intensity of hydration peak (mW/g)	Age of hydration peak (h)	Experimental hydration heat at 72h (J/g)	Calculated hydration heat at 72h (J/g)
100PC	4.92	7.76	213.39	213.39
5 TB	4.62	7.75	190.25	200.26
10 TB	4.62	7.75	182.62	202.91
15 TB	4.67	7.14	183.76	216.19
20 TB	4.64	6.88	182.33	227.91
5 T300	4.64	7.74	215.87	227.23
10 T300	4.62	7.47	216.00	240.00
15 T300	4.65	7.21	205.77	242.08
20 T300	4.53	7.13	200.91	251.14
5 T500	4.62	7.75	190.25	200.26
10 T500	4.62	7.73	183.87	204.30
15 T500	4.62	7.73	183.76	216.19
20 T500	4.62	7.73	133.02	166.28
5 T670	4.64	7.88	213.74	224.99
10 T670	4.67	7.47	216.50	240.56
15 T670	4.77	6.92	203.15	239.00
20 T670	4.90	6.26	204.98	256.23
5 T860	4.68	7.58	206.31	217.17
10 T860	4.77	7.18	211.18	234.64
15 T860	4.88	6.67	209.38	246.33
20 T860	4.92	6.01	208.77	260.96
5 CBC	5.39	5.90	222.16	233.85
10 CBC	5.04	6.99	218.73	243.03
15 CBC	5.02	7.18	212.51	250.01
20 CBC	4.93	7.32	212.68	265.85
BIL	4.72	7.55	218.90	243.22
CBL	4.60	7.69	214.96	238.84
10L	4.64	8.17	218.90	243.22

Calcination: T300 and T500

The intensity of the maximum rate of heat, its time of occurrence, the final heat released and the calculated heat for the T300 and T500 pastes shown in Table 3 are much lower than those measured for the control paste. In addition, the values recorded are higher in the T300 pastes than in the T500 pastes, which align with those of TB pastes.

Mixtures incorporating calcined pozzolan exhibit a slight reduction in the induction period and show a higher heat of hydration during this period as compared to the control system [42].

The cumulative heat of hydration at 72 hours in the T300 pastes exceeds that of the TB pastes, which surpasses that of the T500 pastes. This implies that calcination at 300 °C makes the tuff more reactive and more mobilizable in hydration reactions than calcination at 500 °C. This may be related to the higher specific surface area of T300 tuff, even though the literature does not observe any direct or generalized correlation between specific surface area and reactivity [43].

It should be noted that the 20 T500 paste exhibits both the lowest intense heat flux peak and the lowest experimental and calculated heat of hydration, which are 133.02 J/g and 166.28 J/g, respectively.

Prolonged grinding: T670 and T860

The intensity of the maximum rate of heat increases as the content of tuff and its specific surface area increase. Whereas, the start of the acceleration period and the time at which the maximum rate of heat occurres decrease as the tuff content and the specific surface area increase. Grinding the tuff to high specific surface areas dissipates greater heat flux than that of the untreated tuff, but less than Portland cement alone, whereas the time at which the maximum rate of heat occurs is shortened. Finely ground zeolite decreases the induction period time and accelerates the onset of the maximum rate of heat [13,44].

The heat of hydration of the T670 and T860 pastes is slightly lower than that of the control pastes but remains significantly higher than that of the TB pastes. As shown in Table 3, the calculated hydration heats of the T670 and T860 pastes are greater than those of the 100 PC and TB pastes, and they increase as the tuff content increases. In general, a pozzolan with a large specific surface area produces a very high heat of hydration [45].

The pastes containing prolonged grinding tuff have increased the cumulative heat released after 72 h of hydration as compared to the control paste, which proves the tuff's high chemical solubility and the enhancement of the pozzolanic reaction [8].

Co-grinding with Portland cement: CBC

The intensity of the maximum rate of heat release decreases as the content of co-grinded tuff with Portland cement increases, while the time required for its onset is delayed.

The strong exothermic reactions and the ascending slope of the curves showed that co-grinding the tuff with Portland cement produced a very high heat of hydration that exceeds those of the TB pastes.

The heats of hydration of the 5 CBC and 10 CBC pastes are higher as compared to the control paste. Therefore, to prevent thermal shrinkage, the content of tuff co-grinded with Portland cement is limited to no more than 10%.

Grinding with GGBFS: BIL, CBL and 10L

As shown in Fig. 9 (b), the BIL paste exhibits a slight acceleration in the C_3S hydration, in which the main exothermic peak of heat flux appeares earlier than in CBL, 10 TB, and 100 PC pastes. The addition of GGBFS to the CEM I cement results in a slight acceleration of the hydration of C_3S [46]. However, the GGBFS may have hindered the total extent of cement hydration, shown by the delay of the onset time of the maximum rate of heat and the peak corresponding to the transformation of ettringite into monosulfate in the 10 L paste. This follows the data reported previously by other researchers; the supplementary cementitious materials with low pozzolanic

activity decrease the heat of hydration following the cement replacement and the dilution effect [39]. This result is in contrast to that reported by [36], who found that the heat generation rate of mixes incorporating GGBFS is higher than that of pure Portland cement mixture, attributed to the initiation of the pozzolanic reaction.

The final heat released and the calculated heat (Table 3) are significantly higher in BIL, CBL and 10L pastes than in the 10 TB, and 100 PC pastes. Consequently, thermal shrinkage is to be expected.

During hydration, the pastes containing 5% and 10% of tuff co-grinded with Portland cement (5 CBC and 10 CBC), as well as pastes incorporating GGBFS (BIL, CBL and 10L), release significantly more heat than control cement paste or those containing untreated tuff. A similar result was found in a cement-grinding test with GGBFS [38]. The dilution effect, expressed by a slight shortening of the setting time of these mixtures, was overcome by the nucleation effect at 72 h [36]. This result contradicts the findings of other researchers [20], who found that replacing cement with mineral additions leads to a decrease in the heat of hydration. This phenomenon is directly linked to the dilution effect of mineral additions as well as the fact that pozzolanic reactions release less heat than the hydration of Portland cement.

4.3. Free $Ca(OH)_2$ content

The free $Ca(OH)_2$ content of hardened pastes prepared with the ordinary Portland cement, as well as pastes prepared with different rates of replacement of PC by untreated or treated tuff was determined by thermogravimetric analysis (TGA) at 7, 28 and 90 days, and the results are shown in Fig. 10 (a-d).

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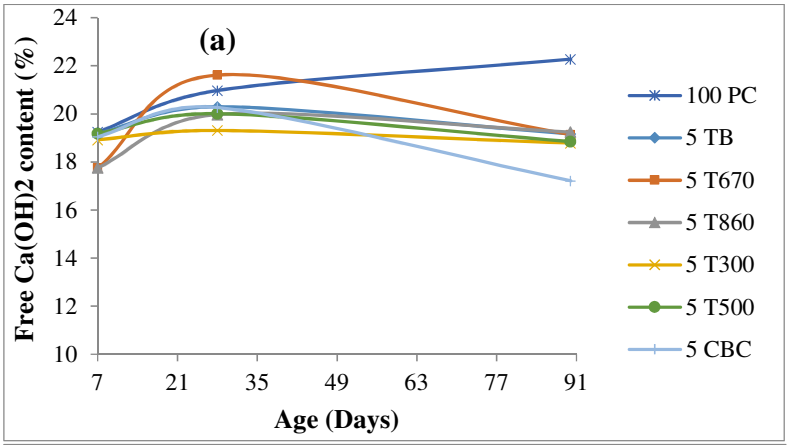

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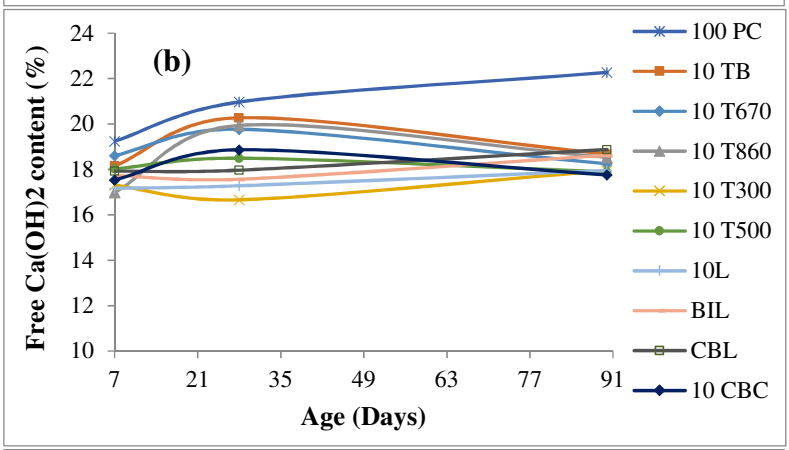

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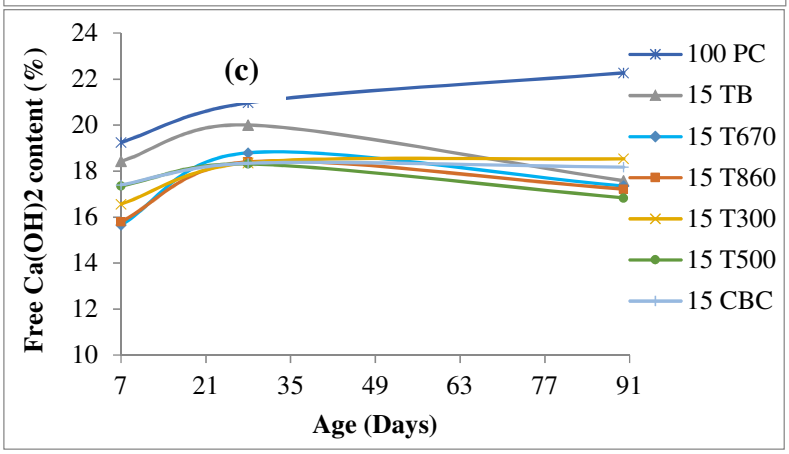

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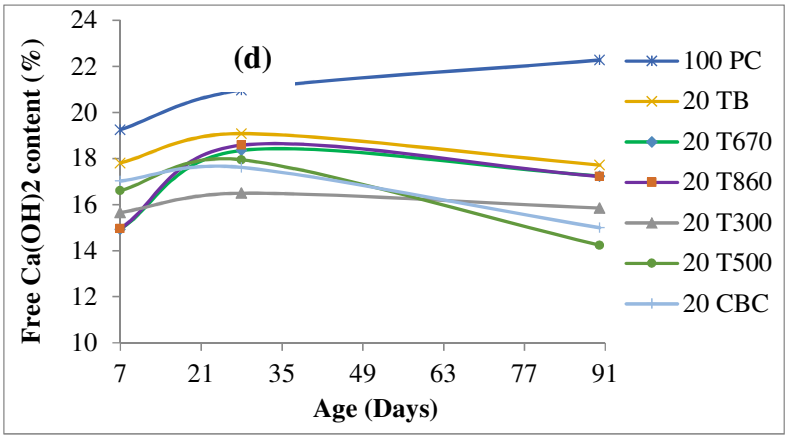

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510 **Fig. 10.** free $Ca(OH)_2$ content of hardened pastes with raw and treated tuff

When comparing the hardened pastes containing raw and treated tuff, it was shown that the content of $Ca(OH)_2$ gradually decreases with the content of activated tuff after 7 days. However, by 28 days, the $Ca(OH)_2$ content of all the pastes had increased but remained lower than that of 100 PC and TB pastes, particularly at the rates of cement replacement by 15% and 20% activated tuff.. Higher $Ca(OH)_2$ content of the pastes at 28 days can be attributed to an enhanced hydration of Portland cement phase in the blended system [30].
At 90 days of age, the free $Ca(OH)_2$ content of all the pastes containing raw or treated tuff decreased. This outcome is related to the pozzolanic reaction in cement systems [32]. The content of free $Ca(OH)_2$ significantly decreases when the replacement rate of Portland cement increases, particularly in the 20 T300, 20 T500 and 20 CBC pastes. Overall, calcination at temperatures ranging from 300 °C to 800 °C resulted in little improvements in the pozzolanicity of the zeolites [23].

The thermal treatment of the tuff at 300 °C confirmed an increase in the pozzolanic activity with respect to the raw tuff as the zeolite (mordenite) destabilised its structure and converted it to a more reactive phase [47]. This outcome is in contrast with the findings of previous research, which reported that calcination of zeolites at temperatures up to 600 °C does not improve pozzolanic reactivity [30]. Other studies have found that thermal treatment of a pozzolan decreases the particle size and the surface area by the aggregation and sintering of the particles, which can result in an insignificant increase or decrease in the pozzolanicity [23,48]. In another study, the authors considered the effect of calcination to be a combination of two opposite effects: an activation depending on the reactivity of the phases and a dis-activation depending on the specific surface area, the decrease in soluble fraction, and the increase in crystallinity [43]. According to some researchers, calcination at 400 °C gives the zeolite better reactivity [49], but others reported that thermal treatment at high temperatures (400–1000 °C) is not recommended as pozzolanic activity decreases [30].
Increasing the fineness of the tuff regardless of the type of grinding (T670, T860 and CBC) did not have a significant effect on increasing pozzolanic activity. This result is also found in the literature [13,32,36,48]. On the other hand, in a previous study, it was revealed that the mechanically activated pozzolan enhanced the capacity to react with calcium hydroxide to form hydration products [50].
Mixtures containing the GGBFS (CBL and BIL) decreased the amount of free $Ca(OH)_2$ content but did not improve tuff reactivity, while$Ca(OH)_2$ consumption remained constant compared to the raw tuff.
The mixture containing GGBFS alone (10L) consumed more Ca(OH)2 than the mixtures containing GGBFS mixed with tuff (BIL and CBL) at the same cement substitution rate of 10%.This observation confirms that the hydration of GGBFS is gradual and continues for longer periods of time [46,51].

The improve of workability in mixtures containing GGBFS was beneficial for the hydration reaction of Portland cement and the production of $Ca(OH)_2$. During this time, the consumption of $Ca(OH)_2$ in the hydration reaction of GGBFS was less than the additional production of $Ca(OH)_2$ by the hydration of Portland cement [52].

4.4. Non-evaporable water content

The non-evaporable water content of hardened pastes prepared with the ordinary Portland cement as well as the pastes prepared with different rates of replacement of PC by untreated or treated tuff was determined by TGA at 7, 28 and 90 days, and the results are shown in Fig. 11 (a-d).

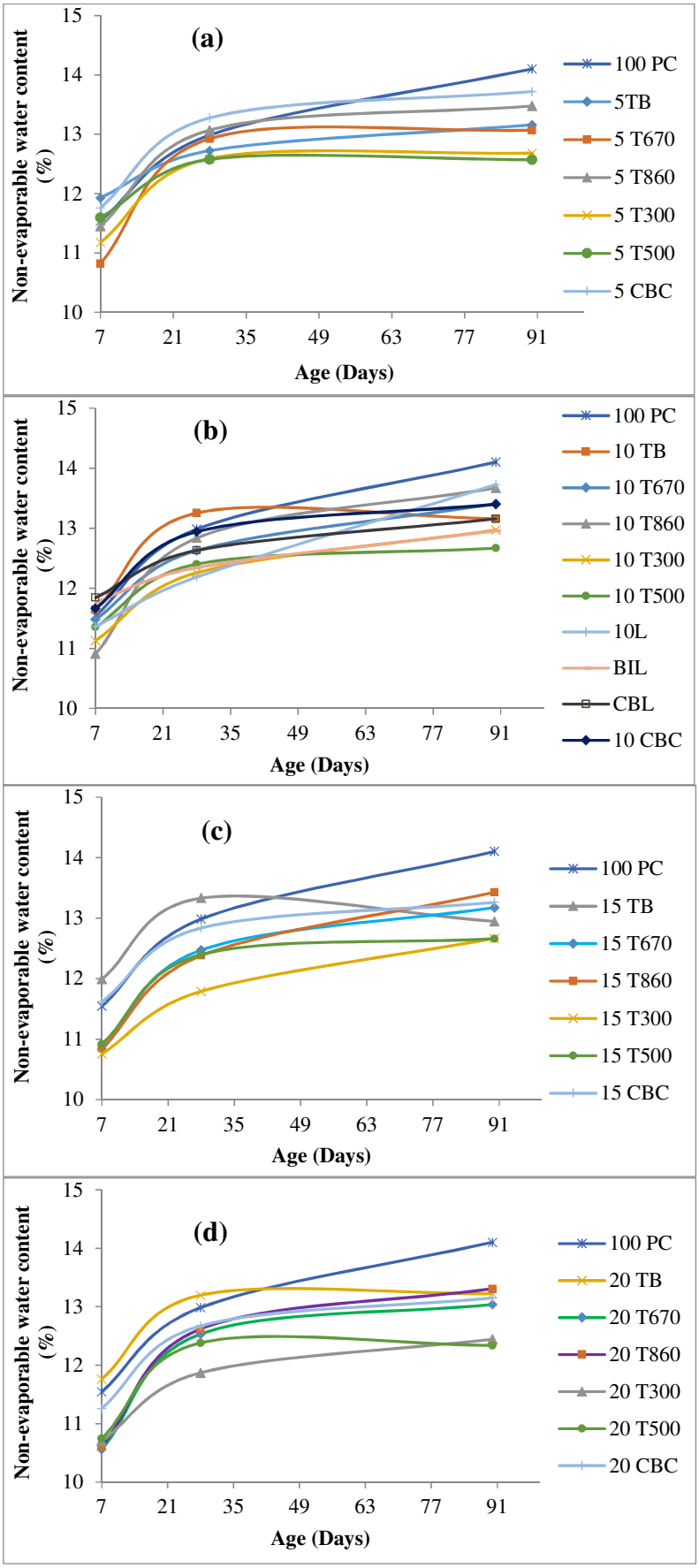


Fig. 11. Non-evaporable water content of hardened pastes with raw and treated tuff

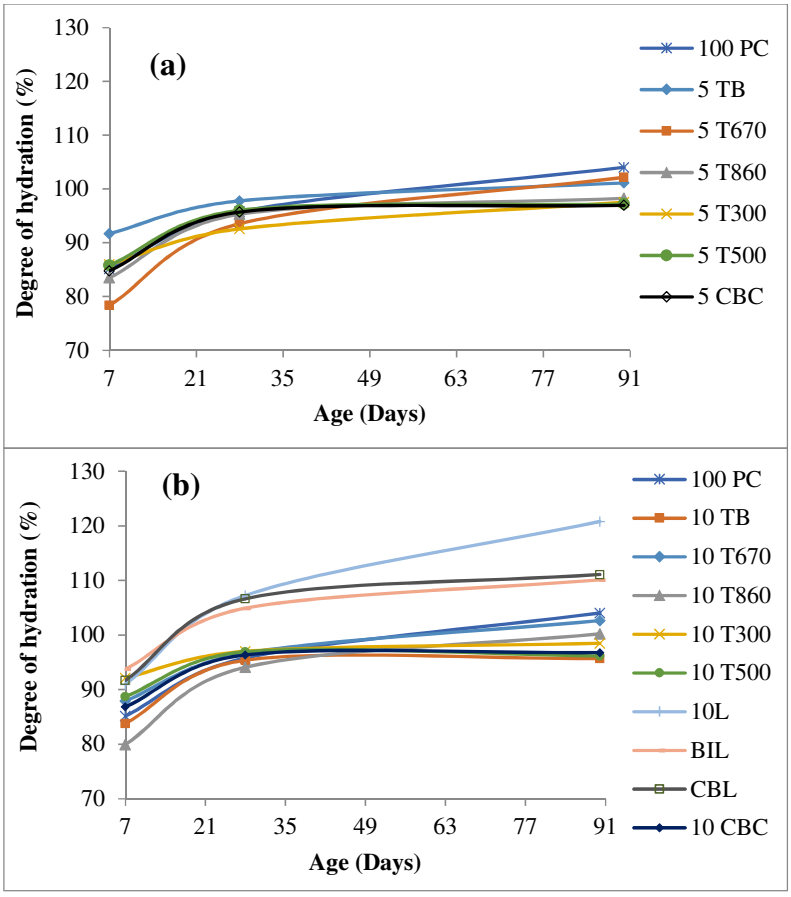
Fig. 11 shows that as the curing age increases, so does the amount of non-evaporable water. Although the hydration reactions are continuous, the kinetic of the non-evaporable water content over time is relatively low. From 7 to 28 days of age, the non-evaporable water content of the pastes containing treated tuff has grown significantly but remained lower than that of 100 PC and TB pastes. At 90 days, the non-evaporable water content continued to increase to exceed, overall, that of TB pastes but remained lower than that of 100 PC. This usually indicates an increase in the overall degree of hydration and can indirectly reflect the hydration products in cementitious systems [46,53,54].

Unlike calcination, mechanical activation resulted in a significant increase in non-evaporable water content. The decrease in the non-evaporable water content may be accompanied by a low degree of hydration of the blended cements, but in a large part, it is due to the dilution of Portland cement in the systems [55].

While increasing the pozzolan content in cement pastes, the non-evaporable water content decreases, and the water combined content in hydrates increases. These results are strongly influenced by the water content of the pastes since the non-evaporable water decreases as the w/b ratio decreases [56].

4.5. Degree of hydration

The degree of hydration of hardened pastes prepared with the ordinary Portland cement as well as pastes prepared with different rates of replacement of PC by untreated or treated tuff was determined by TGA at 7, 28 and 90 days, and the results are shown in Fig. 12 (a-d).



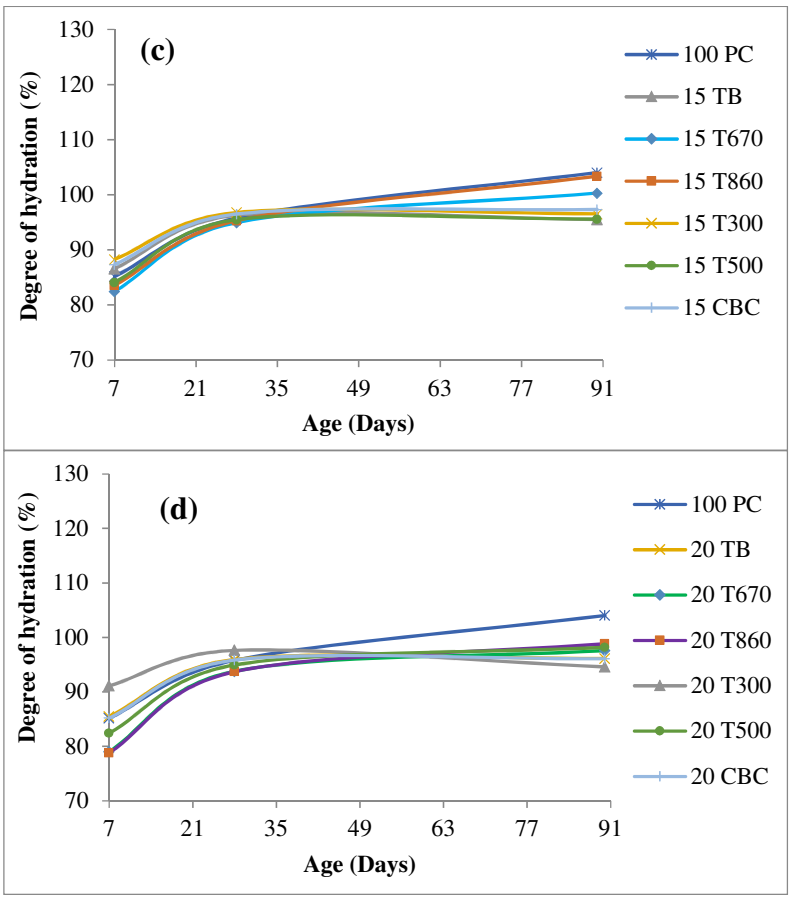


Fig. 12. Degree of hydration of hardened pastes with raw and treated tuff

In Fig. 12, the degree of hydration shows a progressive shape over time, but the activation techniques had no significant effect on the raw tuff nor the Portland cement. Mixtures containing GGBFS showed very high degrees of hydration. For cement substitution rates up to 15%, calcination at 300 °C slightly increases the degree of hydration, but calcination at 500 °C showed no effect. For cement substitution rates up to 15%, prolonged grinding (T670 and T860) of the tuff appears to increase the degree of hydration. The extents of pozzolanic reaction increases significantly due to the finer grain sizes of the ground pozzolans, while the cement hydration is slightly promoted [57]. The degree of hydration was not improved by co-grinding tuff with cement (CBC) to high specific surface areas. Prolonged grinding of a pozzolan decreases its particle size distribution and increases the rate of dissolution, which accelerates the rate of the pozzolanic reaction and therefore increases the degree of hydration [43].

From the figures of non-evaporable water content and degree of hydration, there is no clear correlation nor linear relationship between the two properties. The non-evaporable water content is only an indicator of the degree of hydration since the composition of the hydrates is not precisely known and a certain amount of bound water is lost during the preliminary drying of the samples at 105 °C [31].

Non-evaporable water content in hardened pastes is mainly contributed by cement hydration. Only a very small amount of water will be combined by treated or untreated tuff reactions to form non-evaporable water. Therefore, the amount of non-evaporable water can, to a certain extent, represent the cement hydration degree [57]. But, due to the modifications accommodated by the pozzolan in the quantity of the different hydrates as well as in their chemical composition, the determination of the non-evaporable water content is far from sufficient to determine the degree of hydration of the blended cements [58].

5. Conclusion

The goal of treatment of the raw mordenite-rich tuff was to improve its physical and compositional properties to allow it to react faster or more completely as pozzolans, resulting in improved performance in cementitious systems. Based on the experimental results, it can be concluded that the treatment techniques improve the performance of the raw mordenite-rich tuff. The following are the findings that can be drawn:

Calcination resulted in particle agglomeration, with many of the finer particles becoming adhered to the surfaces of larger particles, which slightly increased the particle size of calcined tuff. Grinding reduces the amount of coarse particles, increases the percentage of the fine fractions, and makes them less agglomerated than in the raw state.

As the tuff content increases, more water is required to make a paste with the same standard consistency as the control paste. Thermal treatment and co-grinding with Portland cement appear to have a minor effect on the water requirement, which appears to grow with prolonged grinding to high specific surface areas. Adding GGBFS to the tuff increased the fictitious ratio of w/b. This is the dilution effect of the mixture, which resulted in the mixture being more workable and much easier to set up.

Calcination extends the initial setting, but accelerates the final setting and the hardening of the cement paste. Regardless of grinding procedure, fine binders (T670, T860 and CBC) exhibited shorter initial and/or final setting time for 5% and 10% tuff content. Furthermore, the slowest final setting was found in pastes containing 15% and 20% of prolonged ground tuff. Incorporating GGBFS had no significant effect on the initial setting but accelerated the final setting. Furthermore, even when just 10% of the cement was replaced by GGBFS and no superplasticizers were used in the paste formulation, the hydration was not retarded. The standard specifications of EN 197-1 limit the initial setting time to a minimum of 45 min. All of the cement pastes meet these requirements.

Pre-treatment of the tuff advances the onset of the acceleration period and greatly accelerates the C3S hydration rate at early stages, resulting in faster and greater hydration heat development than 100 PC and TB pastes. Treated tuff pastes show a shortened deceleration period and an onset time of the heat flux peak corresponding to the transformation of trisolfoalumite to monosulfate. This further highlights the accelerating effect of the treated tuff on the hydration process. After 72 h of cement hydration, the heat flux of the pastes containing treated tuff is much greater than that of 100 PC paste. This demonstrates how activation techniques fully incorporated the treated tuff into the cement hydration reaction.

Thermal treatment of the tuff at 300 °C resulted in an increase in pozzolanic activity compared to raw tuff. Calcination at 500 °C increased the particle size and reduced the specific surface area of the tuff due to particle aggregation and sintering, resulting in a low increase in pozzolanicity. Mechanically activating tuff did not significantly improve its ability to react with calcium hydroxide.

Although the hydration reactions are continuous, the kinetics of the non-evaporable water content over time is relatively low. Unlike calcination, mechanical activation resulted in a significant increase in non-evaporable water content. After 90 days of hydration, pastes incorporating treated tuffs showed non-evaporable water greater than those of TB pastes. This generally indicates an increase in the overall degree of hydration and can indirectly reflect the hydration products in cementitious systems.

Mixtures containing GGBFS showed the highest degrees of hydration. Calcination at 300 °C slightly enhances the degree of hydration, whereas calcination at 500 °C has little effect. Prolonged grinding of the tuff reduces particle size distribution and increases the rate of dissolution, which accelerates the rate of the pozzolanic reaction and therefore increases the degree of hydration, but this case was not shown by co-grinding the tuff with Portland cement.

The findings indicate that there is no evident correlation or linear relationship between non-evaporable water content and degree of hydration. Because the composition of the hydrates is not exactly known and a certain amount of bound water is lost during the preliminary drying of the samples at 105 °C, the non-evaporable water content is only an indicator of the degree of hydration.

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