RESEARCH ARTICLE OPEN ACCESS

Valorization of an industrial waste (sludge) as an artificial pozzolan in cementitious materials

Sanae Lamrani, Laïla Ben Allal, Mohammed Ammari.
Laboratoire des Matériaux et Valorisation des Ressources (LMVR) Faculty of Sciences and Technologies -BP 416 - TANGIER (MOROCCO).

ABSTRACT
The present study fits within the framework of sustainable management of sludge generated from wastewater treatment in industrial network. The studied sludge comes from an industry manufacturing sanitary ceramic products. Physical, chemical and mineralogical characterization was carried out in order to give an identity card to the sludge. We noted the absence of metal pollution. In order to evaluate its pozzolanic character, the industrial sludge has been subjected to thermal activation at various temperatures (from 650°C to 1000°C). The pozzolanic activity was evaluated by physico-chemical and mechanical methods. Pozzolanicity measurement by conductivity, Frattini and Chapelle Test revealed the existence of pozzolanic properties of calcined samples. The best pozzolanic reactivity was obtained for the sample calcined at 800°C. We noticed a decrease in the reactivity of the samples calcined from 850°C. In addition, analysis by means of X-ray diffraction and Fourier transform infrared spectroscopy showed that sludge recrystallization begins at a temperature of 850°C. Pozzolanicity index of the thermally treated samples was determined by measuring the mechanical resistance of mortar specimens previously kept in a saturated lime solution for 28 days. The best pozzolanic activity index was obtained for the sample calcined at 800°C (109.1%). The study of mechanical performances and resistance to chemical attacks of mortars incorporating sludge (calcined at 800°C) with different percentages and at various ages showed an improvement of mechanical and chemical resistance compared to the control mortar (100% cement) . This work is a contribution to the research for new supplying sources of raw materials and additives in the field of construction. It presents a proposition of a promising solution for the valorization of waste material as an additive instead of being discharged into open air dumps causing a major environmental problem.
Keywords: Thermal activation, Industrial sludge, Pozzolanic activity, Valorization, mortars, durability.

I. INTRODUCTION

The residual sludge generated by treatment of industrial effluents in sewage treatment plans are recognized as significant contributors to environmental pollution, their elimination is a major challenge to find a solution that is both economic and ecologic. There are several ways to evacuate this waste; the widely used one in Morocco is landfilling. Among proposed alternative solutions is the use of this waste as a pozzolan in the field of construction (Ahmadi and Al-Khaja, 2001).

According to the standard ASTM C125 (ASTM, 2007), the pozzolan is a siliceous and aluminous material devoid of specific hydraulic properties, but which can react in the presence of water with calcium hydroxide to form compounds exhibiting cementitious properties. Pozzolan can be natural (Pekmezci and Akyüz, 2004; Senhadji et al., 2012) or artificial obtained from industrial by-products (Frías et al., 2008).

The aim of this study is to elaborate a new artificial pozzolan from an industrial sludge coming from a manufacturing industry of sanitary ceramic products. This material was activated by heat treatment; its pozzolanic activity was assessed before and after treatment by direct methods such as Chapelle test, and indirect methods such as strength activity index and conductivity (Donatello et al., 2010). The mechanical (compressive strength) and chemical (resistance to acid attack) performances of this artificial pozzolan as a partial substituent of cement in mortar were evaluated too.

II. MATERIALS AND METHODS

The cement used for this study was the Moroccan CPJ 55 produced by the cement company LAFARGE. Its physical properties, chemical and mineralogical composition data are presented in Table 1.

The industrial sludge used for this research as an artificial pozzolan was obtained in an industry manufacturing sanitary ceramic products. Its chemical composition was carried out by X-ray fluorescence (XRF); the results obtained are given in Table 1. They show that the industrial waste is formed mainly by silica (59.3%) and alumina (26.3%). The mineralogical composition of the sludge was carried out by X-ray diffraction (XRD) and is presented in Figure 1, According to the diffractogram main phases present in the sludge are:

- Kaolinite $Al_2(Si_2O_5)(OH)_4$
- Illite $(K,H_3O)Al_2Si_3AlO_{10}(OH)_2$
- Quartz SiO_2
- Calcite $CaCO_3$

The physicals properties of the pozzolan are given in Table 1.

Table 1. : Chemical and physical characteristics of cement (CPJ 55) and industrial sludge.

	Raw sludge	**CPJ 55**
Chemical composition (%) (XRF)		
SiO_2	59.30	20.53
Al_2O_3	26.30	4.73
Fe_2O_3	0.39	3.21
CaO	0.99	62.71
MgO	0.45	1.94
Na_2O	0.58	0.06
K_2O	1.16	0.73
SO_3	0.09	2.17
LOI	5.00	3.57
Mineralogical composition (Bogue calculation)		
C2S (%)		
C3S (%)	-	14.30
C3A (%)	-	59.07
C4AF (%)	-	7.84
	-	10.47
Physical properties		
Specific gravity (g/cm^3)	2.30	3.06
Specific Surface area (Blaine) (cm^2/g)	7944	3437
Medium particle size (µm)	4.18	-

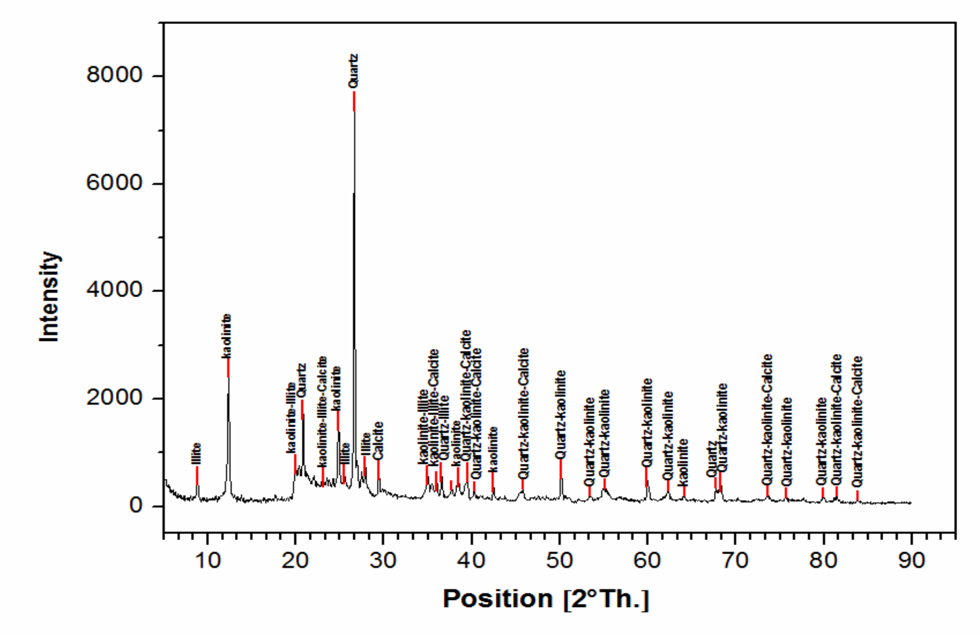

Fig 1. X-ray diffraction pattern for raw sludge

Traces elements were assessed by inductively coupled plasma-mass spectrometry (ICP-MS). Table 2 gives the obtained concentrations. The results show that the sludge doesn't exhibit high concentrations of heavy metals. The content of heavy metals was compared to the allowable threshold values (NF U44-041) standard (NF U, 1989) and the (Decree of December 8, 1997) about the sewage sludge.

We found that the content in trace elements was lower than the threshold values.

Table 2.: Concentration of heavy metals in raw sludge in mg/kg on dry material compared with threshold values of sewage sludge.

Trace elements	**Raw sludge (mg/Kg on dry material)**	**Decree of December 8, 1997 (mg/Kg on dry material)**	**Standard NFU 44-041 (mg/Kg on dry material)**
Cr	**54,54**	**1000**	**2000**
Cu	**32,65**	**1000**	**2000**
As	**36,14**	**-**	**-**
Ni	**31,96**	**200**	**400**
Zn	**2180**	**3000**	**6000**

2.1. Thermal activation and pozzolanic activity tests

In order to obtain amorphous material; the raw sludge was subjected to heat treatment at different temperatures of 650, 700, 750, 800, 850, 900, 950 and 1000°C for 5 hours, the obtained samples were labeled Bcal650, Bcal700, Bcal750, Bcal800, Bcal850, Bcal900, Bcal950, Bcal1000, respectively, and the raw sludge was labeled Bbrut40. They were characterized by XRD and Fourier transform infrared spectrometry (FTIR) and their pozzolanic activity was evaluated by various methods; Chapelle test, Frattini test, electrical conductivity and strength activity index (SAI).

2.1.1. Chapelle test

The aim of the Chapelle test is to determine the amount of lime fixed by the material tested in specific conditions by measuring the amount of residual calcium hydroxide by titration (Pichon, 1994). The test involves heating a solution of 1 gram of CaO and 1 gram of pozzolanic material mixed with 200 ml of deionized water at 90°C for 16 h, the suspension is then filtered and the filtrate is analyzed for Ca^{2+} by titration with Ethylene diamine tetra-acetic acid (EDTA) solution, the result expressed in mg $Ca(OH)_2$ fixed by the studied material.

2.1.2. Frattini test

For this test, the procedure used is specified in EN 196-5 (NF EN, 2006a); 20g of test samples were prepared consisting 80% of CPJ and 20% of the pozzolanic material and mixed with 100ml of deionized water. After preparation, samples were left for 15 days in a sealed plastic bottle in an oven at 40°C. After 15 days, samples were filtered and allowed to cool to ambient temperature in sealed Buchner funnels. The filtrate was analyzed for $[OH^-]$ by titration against dilute HCl with methyl orange indicator and for $[Ca^{2+}]$ by pH adjustment to 12.5, followed by titration with 0.03 mol/1 EDTA solution using Patton and Reeder indicator.

Results are presented as a graph of $[Ca^{2+}]$, expressed as equivalent CaO in mmol/1 on the y-axis versus $[OH^-]$ in mmol/l on the x-axis. The solubility curve of Ca $(OH)_2$ is plotted. Test results lying below this line indicate removal of Ca^{2+} from solution which is attributed to pozzolanic activity. Results lying on the line are indicative of zero pozzolanic activity and results above the line correspond to no pozzolanic activity.

2.1.3. Electrical conductivity test

The objective of the test is to classify pozzolanicity material depends on its effect on the electrical conductivity of a water-lime system, because there is a good correlation between the pozzolanic reactivity of the material immersed in a solution of lime and the decrease in conductivity of this solution. The principle of this method considered as a rapid and efficient (Luxan M P Madruga F Saavedra J, 1989) is to measure the conductivity of a saturated solution of lime in a water bath thermo-stated at 40°C before and after addition of 5g of the studied material (pozzolan), and calculate the difference. The conductivity of lime-pozzolan-water system stabilizes after 2 minutes.

2.1.4. Strength activity index (SAI)

The strength activity index is the most representative judgment strategy for the pozzolanic activity evaluation (Sinthaworn and Nimityongskul, 2009), it was determinate according to ASTM C618 (ASTM, 2003), it's the ratio of the compressive strength of mortar test specimens prepared with 20% artificial pozzolan-80% CPJ mixture, to that of control specimens prepared with 100% CPJ according to EN 196-1 (NF EN, 2006b), all mortars prepared were placed in a saturated lime water bath for 28 days.
The SAI is calculated as in equation 1:

$$SAI\ (\%) = (A/B) * 100 \qquad \text{(Eq 1)}$$

A: The compressive strength of the mortar containing the artificial pozzolan (MPa).
B: The compressive strength of the control mortar (MPa).
ASTM C618 (ASTM, 2003) specifies that the test specimen must have a minimum of 75% of the strength of the control (SAI >75%).

2.2. Substitution of cement by artificial pozzolan in mortars

The preparation of mortars mixtures was realized according to EN196-1 (NF EN, 2006b) the blends were prepared with a constant binder/sand/water proportion of (1/3, 2/3, 0.5) throughout this investigation. The binder consisted of cement and artificial pozzolan, the detailed mix proportion of the mortars are shown in Table 3.

Table 3 : Mixture proportions of mortars prepared.

Code mortars	binders		Sand (g)	Water (ml)
	CPJ 55 (g)	AP (g)		
Control	450	-	1350	225
Bcal800 10%	405	45	1350	225
Bcal800 15%	382.5	67.5	1350	225
Bcal800 20%	360	90	1350	225
Bcal800 25%	337.5	112.5	1350	225
Bcal800 30%	315	135	1350	225

2.2.1. Compressive strength

Prismatic mortar specimens (4*4*16 cm^3) were used for the study of compressive strength. Specimens were cast in steel molds and kept in a moist room at 20+2°C for 24h. Demoulding took place after 24h and specimens were placed in water at 20+2°C for a curing period of 7, 28, 90 days. Each compressive strength value was calculated as the average of the results from three specimens. Compressive strength was determined at 7, 28 and 90 days according to EN196-1 (NF EN, 2006b).

2.2.2. Acid attack

Because the durability of cementitious materials is as important as their mechanical resistance, the performance of mortars containing artificial pozzolan in aggressive media was studied and compared with control mortars according to ASTM C267(ASTM, 2001). The mortars specimens (4*4*16 cm^3) were cured in water at 20 ± 3 °C for 28 days before being subjected to acid attack. Three specimens of each mortar mixture were immersed in 5% sulfuric acid (H_2SO_4), 5% nitric acid (HNO_3) and 5% hydrochloric acid (HCl). The mortar specimens were extracted from the aggressive solutions at 7, 28, 50 and 90 days of immersion and rinsed with deionized water; the chemical resistance was evaluated then by measuring the weight loss of the specimens using Equation 2:

$$\text{Weight loss } (\%) = ((w1 - w2)/w1\ ) * 100$$
(Eq 2)

W1: weight of the mortar before immersion in acid solution.

W2: weight of the mortar after immersion in acid solution.

The acid solutions used were refreshed every 7days and the cumulative weight loss was calculated at 7, 28, 50 and 90 days.

III. RESULTS AND DISCUSSIONS

2.3. Thermal activation and pozzolanic activity tests

2.3.1. X-ray diffraction study

The X-ray diffraction analysis was conducted on the samples calcined at different temperatures to follow the evolution of their mineralogical structures and to determinate the amorphization state of these samples after thermal treatment; the results are presented in Figure 2, the XDR patterns obtained show the following structural transformations:

- At 650°C, all peaks corresponding to kaolinite have disappeared; this means that kaolinite has undergone decomposition process (dehydroxylation) that leads to the disordering of the crystal structure and the transformation to amorphous phase (metakaolinite). Peaks corresponding to calcite have disappeared, from 700°C.
- Quartz and Illite are identified in the XRD patterns of all samples calcined at different temperatures and their structures have not been altered.
- At 850°C, new crystal phase appeared such as Albite and Anorthoclase, at this temperature the sludge recrystallization begins.
- At 1000°C, appearance of peaks corresponding to Mullite (recrystallization of metakaolinite).

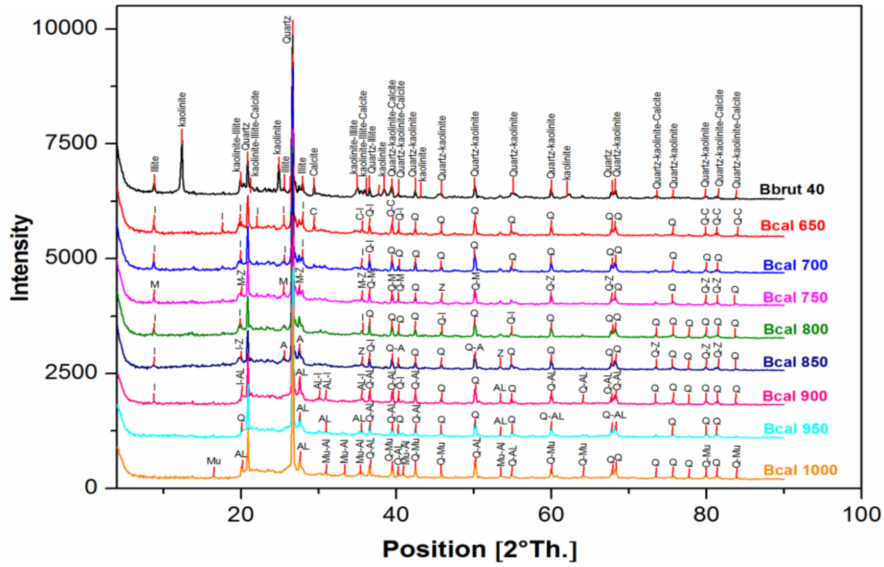

Fig 2. XRD patterns of studied sludge; raw and calcined at different temperatures.

2.3.2. Infrared spectroscopy study

The IR analysis completes the characterization by X-ray diffraction; Figure 3 contains the IR spectrums obtained for the raw and calcined sludge at different temperatures.

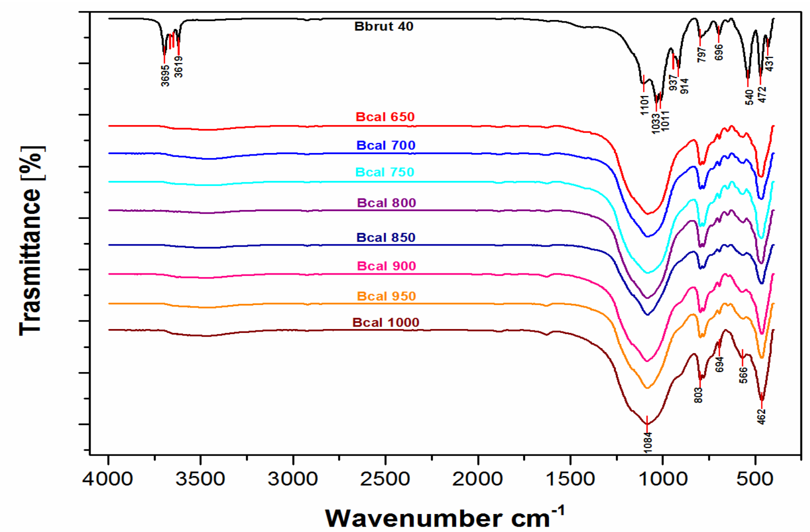

Fig 3. IR spectrum of the raw sludge and calcined at different temperatures (from 650°C to 1000°C).

The spectrum of the raw sludge exhibited the following typical bands for kaolinite:
3694, 3670, 3654 and 3621 cm^{-1} (O–H stretching vibrations); 1106, 794 and 754 cm^{-1} (Si–O–Si stretching and bending vibrations); 1020, 694 and 469 cm^{-1} (Si–O vibrations); 937 and 916 cm^{-1} (Al–OH bending vibrations); and 538 cm^{-1} ($Al^{(VI)}$–O–Si bending vibrations) (Saikia et al., 2003; Van der Marel and Beutelspacher, 1976; Vizcayno et al., 2010).

Heat treatment of the sludge beyond 650°C entails a dehydroxylation by transformation of kaolinite to metakaolin ($Al_2Si_2O_7$), as can be seen in Figure 3; this transformation is characterized by the disappearance of the O-H bands between 3694 and 3621 cm^{-1}, the breaking of bands at 937 and 916 cm^{-1}, associated to Al–OH bending hydroxyl modes (inner surface and inner hydroxyls respectively), and that at 538 cm^{-1} (assigned to Al^{VI}–O–Si), the characteristic bands of the Si-O at 1118 cm^{-1} are transformed into a single large band localized around 1087 cm^{-1}, is a characteristic band of amorphous silica. A new band at 820 cm^{-1} appeared which can be assigned to Al^{IV}–O (Kakali et al., 2001; Rahier et al., 2000).

The results of this analytical technique confirm those obtained by XRD. Indeed, the majority crystalline phases present in the sludge are calcite ($CaCO_3$), kaolinite (Al_2O_3 $2SiO_2$ $2H_2O$), these phases undergo during calcination some decomposition or total disappearance determined by the absence of the characteristic bands.

2.3.3. Strength activity index (SAI):

According to ASTM C 618 (ASTM, 2003), for a material can be used as pozzolanic addition in Portland cement, SiO_2+Al_2O_3+Fe_2O_3 weight must represent at least 70% of total weight; the values of the chemical composition of the sludge presented in Table 1 show that the total silica, alumina and iron oxide content is 85.9% which is higher than the minimum requirement prescribed by the standard.

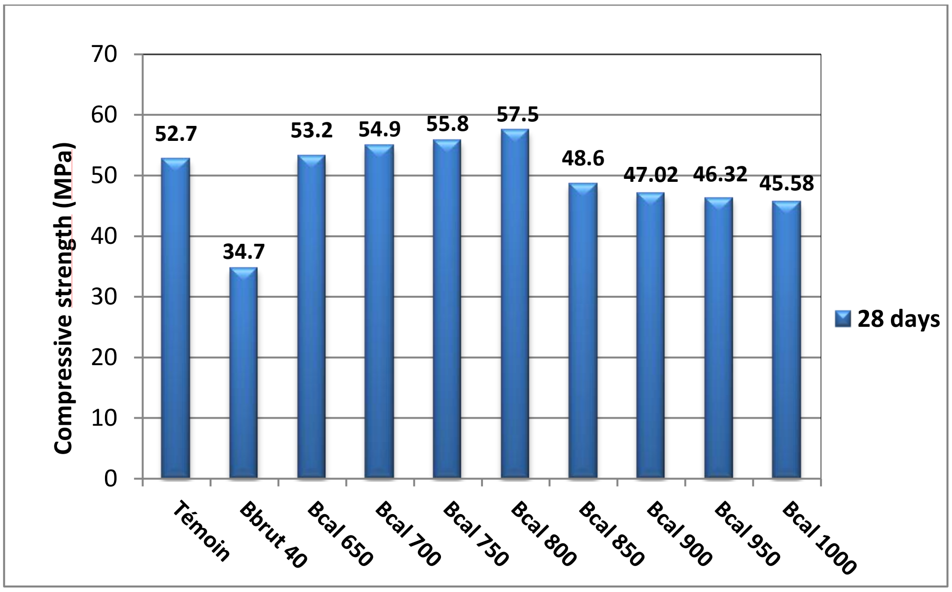

Fig 4. Compressive strength of mortars containing 20% of raw and calcined sludge at different temperatures.

The results of the evolution of the compressive strength of mortar samples stored in saturated lime water are grouped in Figure 4; there is a continuous increase in compressive strength after 28 days for mortars containing calcined sludge at 650-800°C compared to the control; a fall of resistance is registered for the mortar containing the sludge calcined at 850-1000°C.

The strength activity index of the resulting material is a function of his mineralogical composition (Vizcayno et al., 2010). Figure 5 shows that the calcined sludge has a pozzolanic activity whatever the temperature of calcination with a strength activity index higher than 75%, the sludge calcined at 850, 900, 950 and 1000°C show a slight pozzolanic activity, the best result is obtained with the sludge calcined at 800°C (SAI= 109.1%), however the raw sludge show no pozzolanic activity (SAI=65.84%).

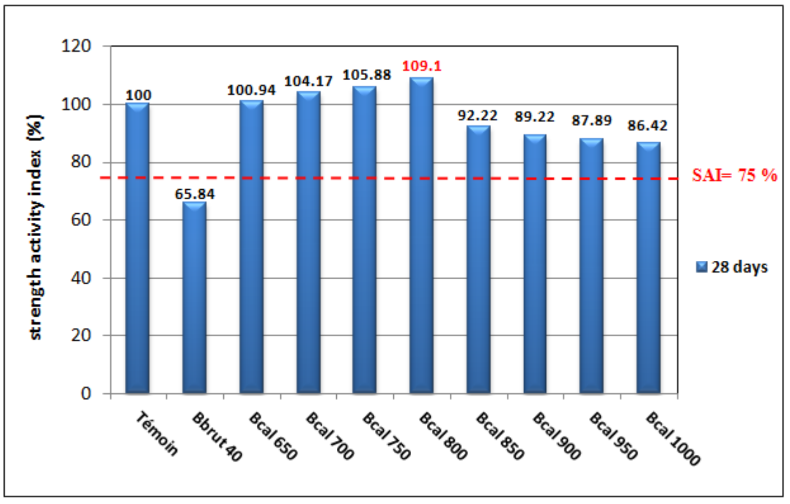

Fig 5. Strength activity index of studied sludge (raw and calcined at different temperatures) after 28 days.

2.3.4. Frattini test:

According to EN 196-5 (NF EN, 2006a), Frattini test consists to prepare samples containing 16g of cement plus 4g of studied sludge mixed with 100ml of deionized water. The results obtained are reported in Figure 6, it indicates that samples containing sludge calcined at 650, 700, 750, 800 and 850 show a positive result because the found concentration of calcium ion in the solution for each sample is lower than the saturation concentration, which means that the sludge calcined at this temperature present a pozzolanic activity. Whereas the raw and calcined sludge at 900, 950 and 1000°C are inactive.

The theoretical maximum [CaO] concentration can be calculated using the formula (equation 3) given in EN 196-5 (NF EN, 2006a) to plot the lime solubility curve.

$$Max\ [CaO] = 350/([OH] - 15)$$
(Eq 3)

The sample calcium concentration [CaO] may be compared to the theoretical maximum [CaO] and the result quantified as the difference between the two values. Result is expressed as a percentage of the theoretical maximum [CaO] removed.

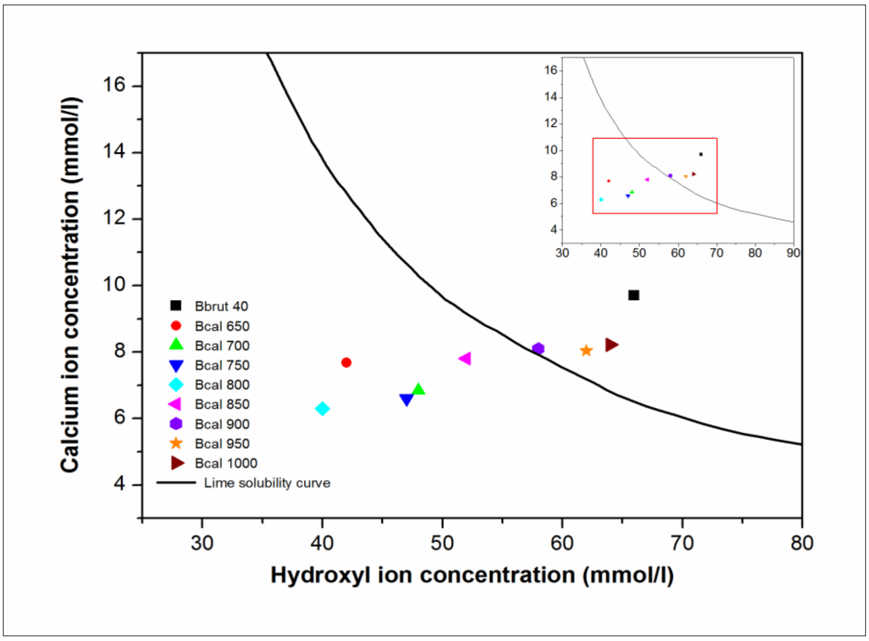

Fig 6. Frattini test results for studied sludge (raw and calcined at different temperatures) after 14 days curing at 40°C

Results presented in table 4 shows that the pozzolanic activity of sludge calcined at 800°C is high with 55% lime removal, and that of sludge calcined at 650, 700 and 750°C is considerable with 40, 35 and 39% lime removal respectively, calcined sludge at 850°C is also active but to a reduced extent with 17.5% lime removal. Raw sludge and calcined at 900, 950 and 1000°C present a negative values of % CaO removal, this results should be normalized to 0% equivalent CaO removal (Donatello et al., 2010) and the samples are considered as not pozzolanic according to this test.

Table 4: Frattini test results for studied samples quantified using Equation 3.

Samples	[OH] mmol/l	[CaO] mmol/l	Theoretical max [CaO] mmol/l	[CaO] reduction %
Bbrut40	66	9.70	6.86	NR*
Bcal650	42	7.68	12.96	40.74
Bcal700	48	6.84	10.60	35.47
Bcal750	47	6.60	10.93	39.61
Bcal800	40	6.30	14	55
Bcal850	52	7.80	9.45	17.46
Bcal900	58	8.10	8.13	NR
Bcal950	62	8.04	7.44	NR
Bcal1000	64	8.22	7.14	NR

*Negative results.

2.3.5. Chapelle test:

In accordance with the Chapelle test, pozzolanic activity of the studied sludge is assessed by the amount of lime ($Ca(OH)_2$) fixed during the pozzolanic reaction. Figure 7 show the amount of calcium consumed by the samples containing raw and calcined sludge at different temperatures.

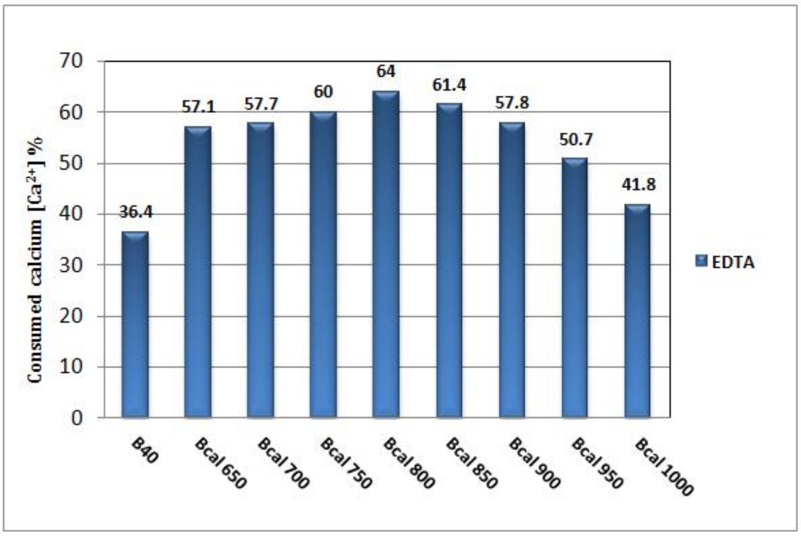

Fig 7. The percentage of consumed calcium by 1g of studied sludge (raw and calcined at different temperatures).

For Bcal650, Bcal700, Bcal750 and Bcal800 samples, pozzolanic activity (fixation capacity of Ca^{2+}) increases with increasing the calcination temperature, it reaches the maximum value of 64% for the calcined sludge at 800°C; this is due to the amorphous structure that obtains the sludge after heat treatment. A decrease in reactivity is observed for samples containing sludge calcined from 850°C, whereas raw sludge can be considered as not reactive.

2.3.6. Electrical conductivity test (EC):

This test is considered as a rapid method for evaluation of pozzolanic activity by conductivity measurement, according to Luxan and al (Luxan M P Madruga F Saavedra J, 1989) the time taken to obtain reliable results is 2 minutes. The results obtained for different samples are presented in Figure 8.

The electrical conductivity of saturated lime solution after adding the studied materials is experiencing a decrease due to the reduction of Ca^{2+} and OH^- ions in the system, which is attributed to the fixation of dissolved $Ca(OH)_2$ by the sludge (raw and calcined at different temperatures).

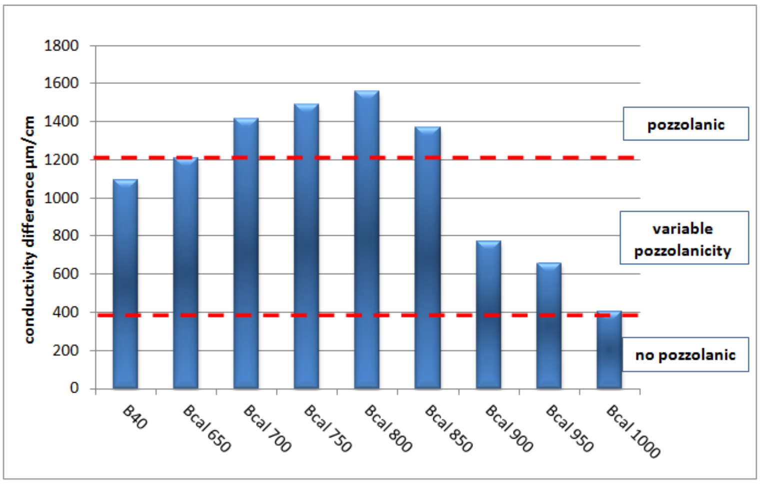

Fig 8. Pozzolanic activity of studied sludge (raw and calcined at different temperatures) determinate by the loss in conductivity.

According to the classification of pozzolanicity by the Variation in conductivity realized by Luxan and al (Luxan M P Madruga F Saavedra J, 1989), sludge calcined at 650, 700, 750, 800 and 850°C are considered as pozzolanic, and raw sludge and calcined at 900, 950and 1000°C present a variable pozzolanicity (conductivity difference between 0.4 and 1.2 mS/cm). The highest reactivity (Δ=1557µS/cm) is attributed to the sludge calcined at 800°C.

2.3.7. conclusion:

The pozzolanicity of the raw and calcined sludge was classified from higher to lower in Table 5, according to the results obtained in each test method used. The calcined sludge at 800°C presents the highest pozzolanic activity for all test methods; this is the optimum calcination temperature of the studied material. At this temperature, the artificial pozzolan presents a great reactivity manifested by the reaction with portlandite (CH) which results from the hydration of cement to form calcium silicates hydrates (C-S-H).

Table 5: Classification of pozzolanic activity of studied sludge (raw and calcined at different temperatures).

Test	SAI	Chappelle	Frattini	EC
↑ +Pozzolanic activity-	Bcal800	Bcal800	Bcal800	Bcal800
	Bcal750	Bcal850	Bcal750	Bcal750
	Bcal700	Bcal750	Bcal700	Bcal700
	Bcal650	Bcal700	Bcal650	Bcal850
	Bcal850	Bcal650	Bcal850	Bcal650
	Bcal900	Bcal900	Bcal900	Bbrut 40
	Bcal950	Bcal950	Bcal950	Bcal900
	Bcal1000	Bcal1000	Bcal1000	Bcal950
	Bbrut 40	Bbrut 40	Bbrut 40	Bcal1000

2.4. Substitution of cement by artificial pozzolan in mortars

2.4.1. Compressive strength:

The compressive strength was selected in order to study the influence of artificial pozzolan (Bcal 800) on the mechanical behavior of blended mortar; Figure 9 shows the evolution of the compressive strength values versus curing time.

The obtained results show that the strength of all mortars increased with age, the substitution of cement with 10, 15, and 20% of artificial pozzolan leads to significant increase in strength in comparison to control mortar from 7 days. This increase is explained by the pozzolanic character of the sludge that reacts with CH during cement hydration to form additional C-S-H, which can fill the pore structure of blended mortar, and thus improving the mechanical properties (Fernandez et al., 2011).

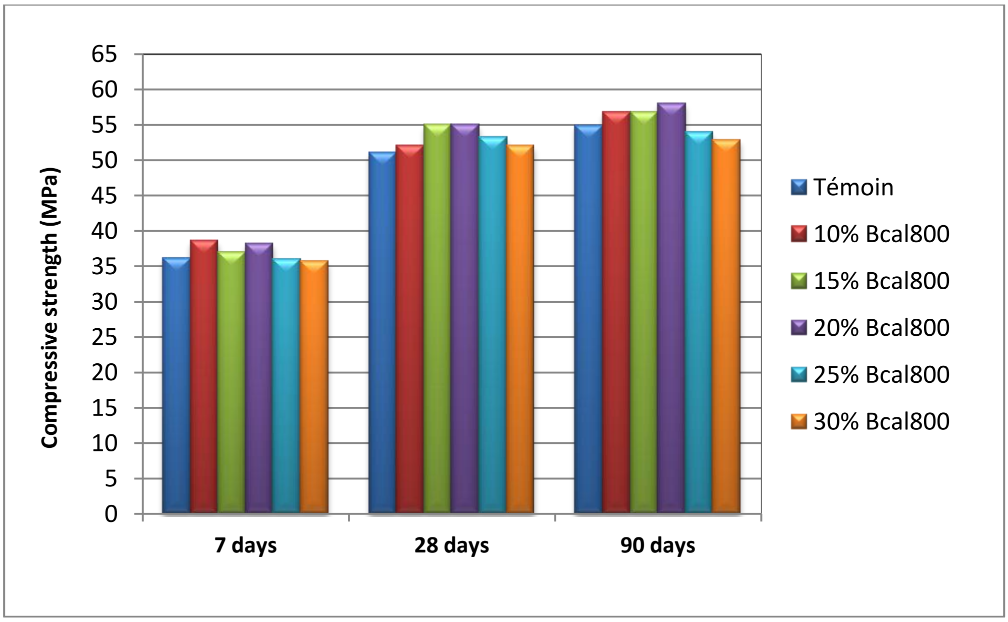

Fig 9. Compressive strength of mortars.

For blended cement containing 25% and 30% of artificial pozzolan, the strength decreases slightly with 1.8% and 3.6% respectively in comparison to control mortar at 90 days, this variation is lower than the percentage of substitution used, which demonstrates that the pozzolanic reaction of activated sludge in this case compensates almost all of the dilution effect.

The best mechanical performance is achieved for blended cement containing 20% of artificial pozzolan with a value of strength 58.5MPa.

2.4.2. Acid attack:

The results of weight loss for specimens exposed to different acid solutions are shown in Figure 10, 11 and 12.

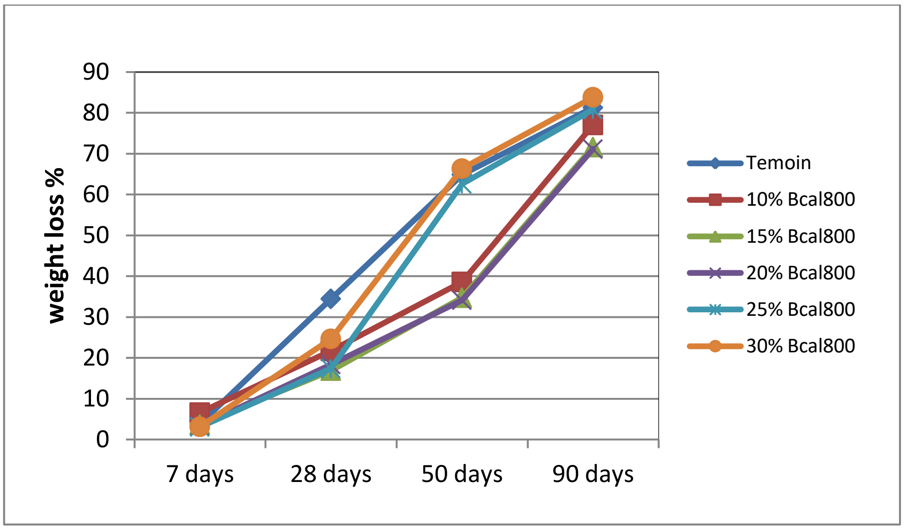

Fig 10. Weight loss of different mortar mixtures immersed in 5% H_2SO_4

For mortars immersed in sulfuric acid (5% H_2SO_4), a continuous loss of weight is observed with time, the results show the same tendency of deterioration for the first 7 days of immersion for all samples, from 28 days the difference became remarkable; the control mortar and mortars containing 25% and 30% of artificial pozzolan exhibit the highest loss of weight equal to 81%, 80% and 83% respectively; This can be explained by the erosive action of the acid solution on the surface of mortars, also the formation of gypsum and ettringite causes expansion and disintegration of cement pastes (Çolak, 2003), followed by mortars containing 10% and 15%, the mortar with 20% of substitution is the less damaged with a weight loss of 71% at 90 days, lower than the control mortar by 12.5%; This chemical resistance to sulfuric acid is due to the pozzolanic reaction responsible of the formation of secondary C-S-H; that are less leachable than the portlandite, thus reducing the amount of the resultant portlandite of cement hydration and increasing densification of the cured paste cement, which makes the penetration of sulphates difficult.

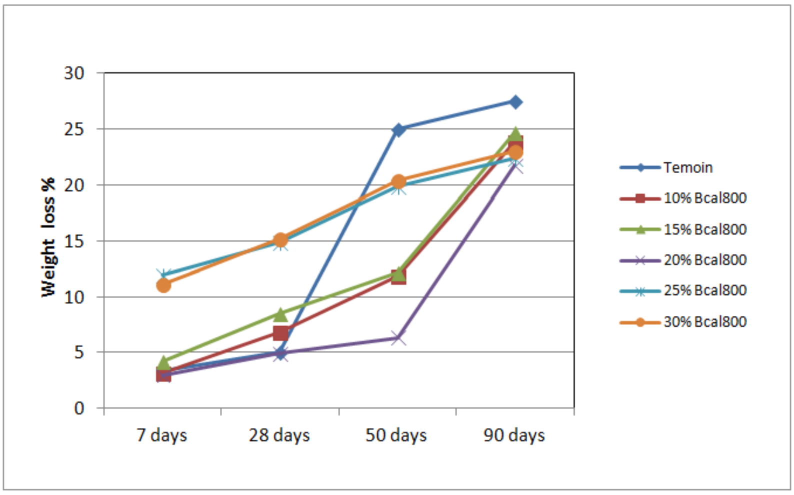

Fig 11. Weight loss of different mortar mixtures immersed in 5% HNO_3.

The results of weight loss of mortar specimens exposed to nitric acid are presented in figure 11, they show that the weight loss of mortars with artificial pozzolan is less than the control mortar at 50 and 90 days; this is caused by the reaction of acid which causes a progressive leaching of portlandite and C-S-H gel. The mortars containing 25% and 30% of artificial pozzolan exhibit a slight increase in the weight loss compared to that containing 20%. As for other tests of durability, mortar with 20% of substituent is the most resistant to this acid attack, its weight loss at 90 days of immersion is 21.7%, lower than that of control mortar by 21%, this is can be attribute to the incorporation of optimal amount of pozzolan in mortar which is responsible of the reduction in quantity of $Ca(OH)_2$, increasing the density and impermeability of the mortar.

Figure 12 show the effect of hydrochloric acid on the mortar specimen, the control mortar presents the biggest weight loss at 50 and 90 days, 22.7% and 24% respectively. For mortars containing 10, 15, 20, 25 and 30% of artificial pozzolan, the reduction of weight loss at 90 days compared to control mortar is 35, 35.5, 36, 13.5 and 12.8% respectively; it is noted that the mortar specimen with 20% of addition present the greater resistance with the lowest weight loss. The partial substitution of cement by the artificial pozzolan in mortar reduces the capillary pores by a secondary C-S-H gel produced by the pozzolanic reaction which improves the resistance of the cement paste against acid attack.

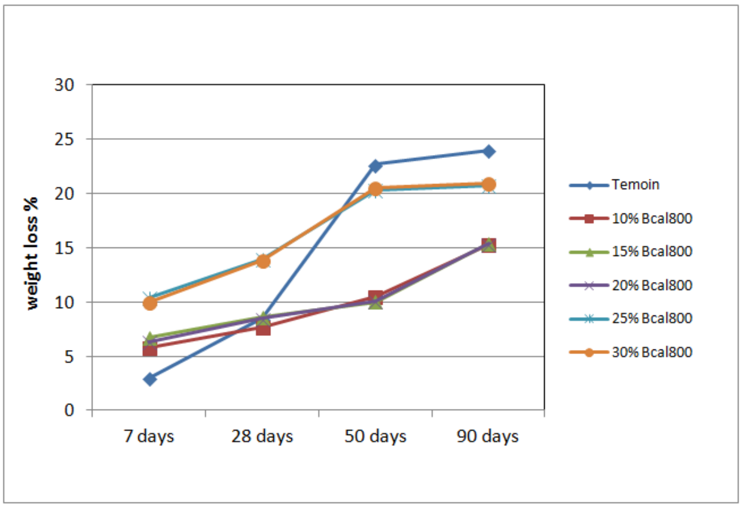

Fig 12. Weight loss of different mortar mixtures immersed in 5% HCl.

By comparing the aggressiveness of sulfuric acid, hydrochloride acid and nitric acid we conclude that the mortars present more weight loss in sulfuric acid than in the other acid solutions, as is clearly seen in figure 13, after 90 days of immersion in 5% H_2SO_4, mortar have totally lost its form (loss of more than half of sample); the abundance of gypsum formed in the surface, facilitates its dissolution in water which explains the mechanism of deterioration of mortar. However, for mortars kept in 5% HCl and 5% HNO_3, a small change is observed.

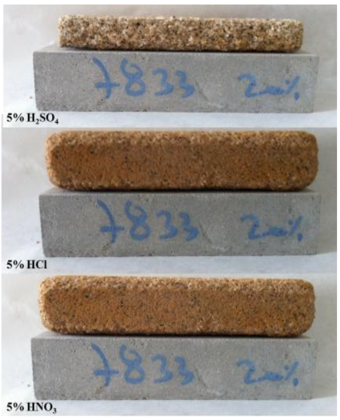

Fig 13. Deterioration of specimens after 90 days of immersion.

The use of this artificial pozzolan with the optimal amount of 20% in mortars improves their resistance against acid attack; several studies in agreement with this work have demonstrated the influence of the partial substitution of cement by pozzolan on the improvement of the durability (Kaid et al., 2009; Makhloufi et al., 2014)

ACKNOWLEDGMENTS

The research was supported by Quality and Environment department in cement company 'Lafarge Cementos' in Tangier, Morocco.

IV. CONCLUSION

The objective of this work was the thermal activation of an industrial sludge, the evaluation of its pozzolanic activity and the study of its influence as a partial substituent of cement on the mechanical and chemical properties of mortars.

The XRD and IR analysis of the raw sludge has shown that it contains mainly Kaolinite, Quartz, Illite and Calcite, after thermal treatment at different temperatures ranging from 650°C to 1000°C, its mineral composition has undergone some decompositions and transformations, from 850°C it was noted the appearance of new crystalline phases (mullite, albite ..), its therefore the beginning of recrystallization temperature. The estimation of the pozzolanicity by several tests such as SAI, Frattini test, Chapelle test and conductivity has shown that calcined sludge at different temperatures exhibits pozzolanic properties with different degrees; according to the results, The optimum calcination temperature is 800°C, at this temperature the activated sludge has the highest pozzolanicity manifested by the high consumption of portlandite during cement hydration with a SAI equal to 109%. The raw sludge is considered as inactive and that calcined at 850, 900, 950 and 1000°C show a low power pozzolanic because of its crystalline structure resulting of thermal treatment at high temperatures (T°C ≥850°C). The activated material at 800°C can be considered as a suitable pozzolanic addition for Portland cements.

Several blended cements were prepared with different percentage of substitution (10, 15, 20, 25 and 30%), the evaluation of mechanical properties has shown that mortars containing 10, 15 and 20% of artificial pozzolan (activated sludge at 800°C) have a higher values of compressive strength than control mortar for all curing times (7, 28 and 90 days), a slight decrease in resistance is recorded for those containing 25 and 30% of addition at 90 days. The optimal pozzolan amount that can be used to achieve maximum strength is 20% of cement replacement which give the value of 58MPa at 90 days, higher than that obtained for control mortar by 8%.

The incorporation of the industrial sludge as addition (cement substituent) in mortars is beneficial to the resistance to aggressive agents. The obtained results showed that whatever the percentage of substitution or acid solution used (5% H_2SO_4, 5% HCl, 5% HNO_3), mortars containing activated sludge are less degraded than that containing only cement, however the values recorded for mortar mixtures with 25 and 30% of substitution are close to that obtained for the control mortar. The optimal percentage which leads to a better resistance to chemical attack is 20%.

Thus the use of this waste as an artificial pozzolan in cementitious materials represents a promising solution that solves the problem of waste evacuation and the creation of new raw material supply resources.

REFERENCES

[1]. Ahmadi, B., Al-Khaja, W., 2001. Utilization of paper waste sludge in the building construction industry. Resour. Conserv. Recycl. 32, 105–113.
[2]. ASTM, 2007. C 125 Standard Terminology Relating to Concrete and Concrete Aggregates. American Society for Testing and materials.
[3]. ASTM, 2003. C 618. Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete. American Society for Testing and materials.
[4]. ASTM, 2001. C 267 Standard Test Methods for Chemical Resistance of Mortars, Grouts, and Monolithic Surfacings and Polymer Concretes. American Society for Testing and materials.
[5]. Çolak, A., 2003. Characteristics of pastes from a Portland cement containing different amounts of natural pozzolan. Cem. Concr. Res. 33, 585–593.
[6]. Donatello, S., Tyrer, M., Cheeseman, C.R., 2010. Comparison of test methods to assess pozzolanic activity. Cem. Concr. Compos. 32, 121–127.
[7]. Fernandez, R., Martirena, F., Scrivener, K.L., 2011. The origin of the pozzolanic activity of calcined clay minerals: A comparison between kaolinite, illite and montmorillonite. Cem. Concr. Res. 41, 113–122.
[8]. Frías, M., García, R., Vigil, R., Ferreiro, S., 2008. Calcination of art paper sludge waste for the use as a supplementary cementing material. Appl. Clay Sci. 42, 189–193.
[9]. Kaid, N., Cyr, M., Julien, S., Khelafi, H., 2009. Durability of concrete containing a natural pozzolan as defined by a performance-based approach. Constr. Build. Mater. 23, 3457–3467.
[10]. Kakali, G., Perraki, T., Tsivilis, S., Badogiannis, E., 2001. Thermal treatment of

kaolin: The effect of mineralogy on the pozzolanic activity. Appl. Clay Sci. 20, 73–80.

[11]. Luxan M P Madruga F Saavedra J, 1989. Rapid Evaluation Of Pozzolanic Activity Of Natural Products. Cem. Concr. Res. 19, 63–68.

[12]. Makhloufi, Z., Bouziani, T., Hadjoudja, M., Bederina, M., 2014. Durability of limestone mortars based on quaternary binders subjected to sulfuric acid using drying–immersion cycles. Constr. Build. Mater. 71, 579–588.

[13]. NF EN, 2006a. NF EN 196-5: Méthodes d'essais des ciments – Partie 5: Essai de pouzzolanicité des ciments pouzzolaniques (April). Comité Européen de Normalisation, AFNOR, Paris FRANCE.

[14]. NF EN, 2006b. NF EN 196-1: Méthodes d'essais des ciments–Partie 1: détermination des résistances mécaniques (April). Comité Européen de Normalisation, AFNOR, Paris FRANCE.

[15]. NF U, 1989. NF U 44-041, Boues des ouvrages de traitement des eaux usées urbaines, dénomination et spécification, norme homologuée. AFNOR, Paris.

[16]. Pekmezci, B.Y., Akyüz, S., 2004. Optimum usage of a natural pozzolan for the maximum compressive strength of concrete. Cem. Concr. Res. 34, 2175–2179.

[17]. Pichon, H., 1994. Le système "pouzzolanes naturelles-chaux-eau" à 38 et 100[C] : relations entre la réactivité chimique, les phases néoformées et les conséquences physico-mécaniques (application aux matériaux volcaniques du Massif Central français. Thèse de Doctorat de l'université joseph fourier, Grenoble I.

[18]. Rahier, H., Wullaert, B., Mele, B. Van, 2000. Influence of the degree of dehydroxylation of kaolinite on the properties of aluminosilicate glasses. J. Therm. Anal. Calorim. 62, 417–427.

[19]. Saikia, N.J., Bharali, D.J., Sengupta, P., Bordoloi, D., Goswamee, R.L., Saikia, P.C., Borthakur, P.C., 2003. Characterization, beneficiation and utilization of a kaolinite clay from Assam, India. Appl. Clay Sci. 24, 93–103.

[20]. Senhadji, Y., Escadeillas, G., Khelafi, H., Mouli, M., Benosman, A.S., 2012. Evaluation of natural pozzolan for use as supplementary cementitious material. Eur. J. Environ. Civ. Eng. 16, 77–96.

[21]. Sinthaworn, S., Nimityongskul, P., 2009. Quick monitoring of pozzolanic reactivity of waste ashes. Waste Manag. 29, 1526–1531.

[22]. Van der Marel, H., Beutelspacher, H., 1976. Atlas of infrared spectroscopy of clay minerals and their admixtures. Elsevier. 350pp.

[23]. Vizcayno, C., de Gutiérrez, R.M., Castello, R., Rodriguez, E., Guerrero, C.E., 2010. Pozzolan obtained by mechanochemical and thermal treatments of kaolin. Appl. Clay Sci. 49, 405–413.