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Characterization and valorisation of sludge of wastewater treatment plant (WWTPs) into cement industry

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Abstract

In Municipal sewer sludge production in EU is expected to rise to 13.0 million tons in 2020. Also in Algeria the estimated quantity of sludge produced in 2017 will exceed 2.0 million tons per year. Since there production, the treatment and disposal of sewage sludge is become an economically and environmentally sensitive problem. The challenge facing sludge managers is to find cost-effective and innovative solutions whilst responding to environmental, regulatory and public pressures. Methods were developed for reducing and disposal the quantities of generated sludge. The present paper is a contribution to valorizing the ashes sludge of wastewater treatment plants (WWTPs) for the production of a green-cement. Mineralogical and physic-chemical characterizations of ashes sludge were carried out. Ashes contain significant amounts of Al_2O_3 and SiO_2 and can be used as a partial replacement of clinker. Four green-cement samples were prepared by substitute (5, 10, 15 and 20%) of ashes into cement standard. Mechanical tests (compressive strength and bending tensile strength) were carried out to the sample mortars (40x40x160mm^3) made of green-cements at different curing times (2, 7 and 28 days). The results show that after 28 days of curing, the compressive strength exceeds 50 MPa. The same trend is observed with specimens tested in bending tensile strength exceeding 7 MPa. These results are encouraging for better management of sludge from Algerian plants in the field of cement industry.

1. Introduction

Wastewater treatment in all parts of Europe has improved during the last 15-20 years in consequence of Urban Waste Water Treatment Directive 91/271/EEC. Over the 80-90% of the population of northern, central and southern Europe is connected to a WWTP and a tertiary treatment is implemented in the 74% of EU plants located in urban areas exceeding 150,000 inhabitants [1]. Municipal sewer sludge production in EU-27 was estimated at 11.5 million tons of dry solids for 2010 and it is expected to rise to 13.0 million tons in 2020 [2]. In Algeria, the National office of Cleansing (ONA: Office National d'Assainissement) manages 96 WWTPs (until 2013). Total quantity estimated of sludge produced summers 1.97 million tons per year [1]. There is a strong

need of perspective which is technically feasible and economically favourable for WWTP managing companies, as well characterized by a positive environmental balance [3]. Several ways exist for the elimination of this sludge, but the choice remains often related to the cost of the installation, the origin of the sludge, the added-value of the products which results from this and the impacts of the solution retained on the environment.
Among the solution retained to treat the sludge, we can cite the production of biogas as a source of heat and electricity on the one hand, and agricultural valorisation in the production of fertilizer and compost on the other hand. These solutions constitute clean technologies which minimize the risks of pollution. The agricultural valorisation of sludge after composting, contributes to a rehabilitation of mineral and organic elements in the soil. This transformation will make it possible to approach the natural cycles in the grounds [4]. The pollutants in the compost of sludge, in terms of heavy metals and organics, must be lower than predefined limits [5]. Also, the use of sewage sludge as an alternative fuel was proposed in the clinkering process in Portland cement industry [6-7]. Other fields of valorisation of sludge from WWTPs are explored during the last two decades. In Algeria three major ways of elimination of sludge are agriculture, storage and landfill (see Fig. 1) [8]. Most of the recent works explore the heat treatment to reduce the volume of the sludge and to stabilize the mineral phases [9-10-11-12]. Without denying the interest of the ways of valorisation quoted above, those consistent to incorporate them in the production of ecological cements constitute an ecological and economical solution. The use of such materials which are mostly considered as industrial wastes or by products, leads to a significant reduction in CO_2 emissions [13-14-15-16-17-18]. Indeed, world consumption of the cement strongly increases during the last twenty years, with an average rhythm of increase higher than 5% a year. The demography, the urbanization and the economic growth, increase the needs in housing and infrastructure in the building and public works sectors. Moreover, according to researchers and cement producers, the manufacturing of cement is strongly energy-consuming and has a harmful environmental impact. The valorisation of dried sludge (dryness > 92% SM) from WWTPs could contribute to the reduction of the need in energy for cement-manufacturers. The organic matters of sludge improve the calorific power considerably. The introduction of sludge into new cement can allow reduction of CO_2 emission.

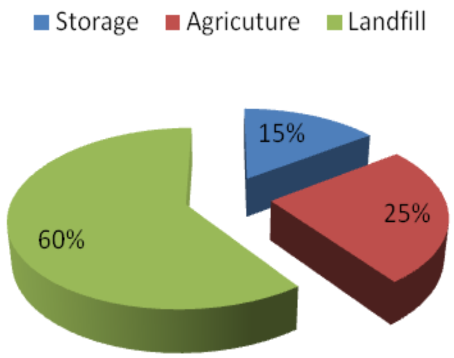

Figure 1: Ways of elimination of sludge in Algeria [8].

The present study describes a new way of sludge management from WWTPs by valorising the latter in the manufacturing of ecological and economical cement (green-cement).
In this work, after a detailed characterization of raw and calcified sludge of WWTPs, various composition of the green-cement (with increasing amount of substitution in the raw cement) was tested. To evaluate the performance of the new binders, prismatic samples made of mortars were carried out and tested in compression and in flexion. The mechanical characteristics measured at different ages instead of different issues (2, 7 and 28 days) show the ability of the new binders.

2. Experimental details

To explore the viability of the proposed valorisation of ashes of sludge, the methodology proposed in this work is composed by three levels (see Fig. 2). The first level concerns the characterization of the sludge. The second level of the methodology deals with the characterization of the designed green-cement. Finally, in the third level, the green-cement performance, in regards to the mechanical behaviour, is evaluated throughout tests on prismatic specimens in compression and flexion.

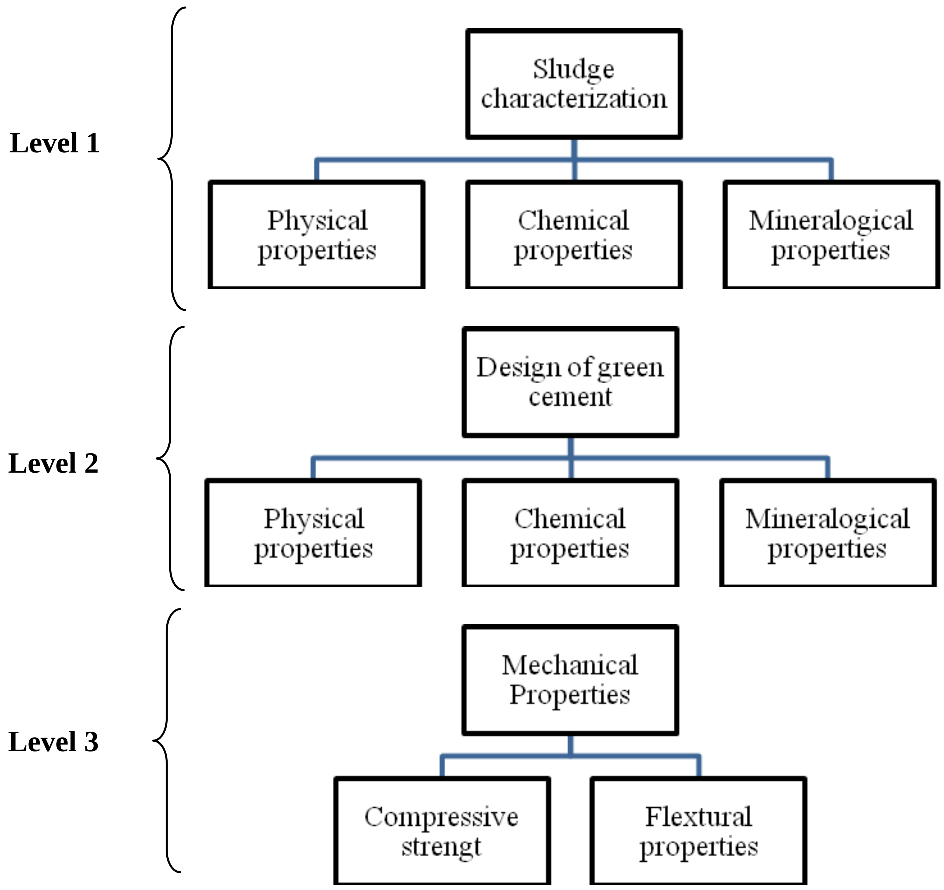

Figure 2: Methodology of the study.

The samples of the studied sludge drying bed were taken from the WWTPs in the district of Sidi Bel Abbes (a city in the west of Algeria, 400 km from Algiers (Algeria)). The samples were stored at a temperature of - 4 °C in order to eliminate any risk of fermentation. Physical parameters of the sludge such as: the amount of dry volatile matters (DVM), the amount of humidity, the amount of dry matter (DM), the organic matter content (OM), the amount of mineral matter (MM), dry apparent density and the Methylene blue value (MBV), are measured in accordance with French standards as shown in Tab. 1.

Table 1: Standards used to characterize the physical properties of the WWTPs sludge.

Property	Test standard
Loss on ignition of dry mass	EF EN 12879
Particle density and water absorption	EF EN 1097-6
Dry matter	NF U 44-171
Loss on ignition in waste, sludge and sediments	NF EN 15169
Methylene blue of soil by means of the stain test	NF P 94-068

The chemical characterization of sludge in terms of metal trace elements (MTE) is an important parameter. This is true especially when the valorisation is in the field of cement like substitution. In this work, the characterization was carried out on the sludge by using the preparation method described in the standard NF ISO 11464 (X31-412). The MTE were quantified by using the adequate techniques of atomic spectrometry.
To explore the transformations generated by heat treatment on the studied sludge, a thermal analysis by differential scanning calorimeter was realized. The equipment used is of type DSC 92. During this test, the slope of increase in the temperature used is 10°C/min. This analysis was realized under an inert gas (nitrogen).
Ashes were obtained by calcified the sludge of WWTP (previously dried at 105°C) in muffle furnace Nabertherm L 5/11 under a temperature of 550 °C for a period of 4H. The texture of the calcified sludge

produced was studied in their natural state, using environmental scanning electron microscope (SEM). An X-ray diffraction analysis was undertaken to these ashes sludge, using Oxford 1000 MDX (Multi-dispersive X-ray fluorescence analyzer element).
The preparation of the green-cement was made in the laboratory of the cement factory of Zahana (district of Mascara, west Algiers). From the components, to prepare the cement, the duration of crushing (in regards to Blaine specific area) was fixed to three minutes on the bases of standard cement preparation. The compositions of studied green-cements are given in Tab.2.

Table 2: Composition in mass of different green-cement prepared.

Cement	Gypsum (%)	Clinker (%)	Ash (%)
EC0	5	95	0
EC5	5	90	5
EC10	5	85	10
EC15	5	80	15
EC20	5	75	20

In terms of the development and analysis of the green-cement properties, the experimental program comprises Blaine surface measurements, chemical and mineralogical analysis. To evaluate the performance of the developed green-cement, prismatic samples (40x40x160 mm^3) of a mortar made of the green-cements and standard cement were tested. The mortar used is composed in mass, of one part of cement (or green-cement), three parts of standard sand and a half part of water (in masse water/ cement is equal to 0.5).
Each batch for three test specimens comprises 450 g ± 2 g of cement, 1350 g ± 5 g of standard sand and 225 g ± 1 g of water. In total forty-five prismatic specimens were prepared.

3. Results and Discussion

The physical characteristics of the studied sludge are shown in Tab.3. From these results, it is to note the high water content, the high OM (≈ DVM) levels and a relatively low value of methylene bleu value. Compared with the characteristics of other WWTPs sludge, these values are relatively comparable [19].

Table 3: Physical characteristics of the sludge from WWTPs

Property	Value
Dry matter (%)	85.11
Dry volatile matter (% DVM)	39.87
Mineral matter (% DVM)	60.13
Humidity (%)	14.88
Particle density	0.69
Methylene blue of a soil by means of the strain test	0.85

In terms of chemical characteristics, on Tab.4, the contents of metal trace elements in the sludge studied were compared with the limit values defined in the standard NF U 44- 051. The results presented in Tab.4 show that the sludge contains a low metal trace elements compared to the thresholds in the standard NF U 44- 051 and the values proposed in other studies [19-20].

Table 4: Chemical compositions sludge studied.

Element	Cd	Cr	Cu	Ni	Pb	Mg	Zn
Limite value of MTE	10	1000	1000	200	800	10	3000
Studies sludge (ppm)	nd*	100.5	189	nd	nd	4.06	142.5

nd*: not determined.

The thermogram obtained by differential scanning calorimetry (DSC) of the studied sludge is presented in Fig.3. The analysis of this thermogram shows the transformation of studied sludge in two processes: endothermic and exothermic between 120 °C and 500 °C. There may also be a phase transformation between 230 °C and 280 °C. Reactions take place at lower temperatures being mainly CO_2 and H_2O, with little amounts of CH_4, as it expected for mainly total oxidation reactions [21]. A little endothermic peak corresponding to water vaporization is observed for the studied sludge at temperatures lowers than 200°C. Two exothermic peaks are observed between 200 and 500°C, which correspond to the combustion. According to the suggestion by [22-23-11], the first peak corresponds to the oxidation of biodegradable matter and the second one will be mainly due to the oxidation organic polymers from the sludge or from dead bacteria.
From 500 to 600°C the mass loss is negligible indicating that no biodegradable matter that burns only at temperatures higher than 550°C [21].

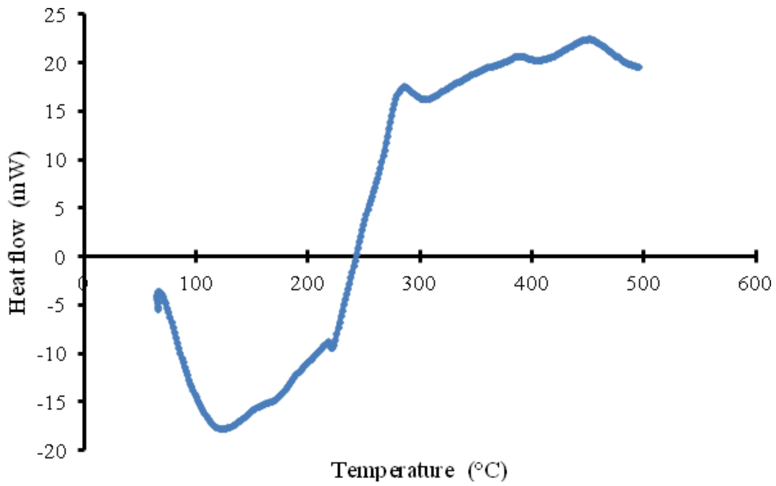

Figure 3: Thermogram mud studied.

In terms of the observations using an environmental scanning electron microscope, Fig.4 shows the different forms of studied sludge. The images obtained show particles of different shapes and sizes. However, an important part of these particles are in the form of plates (E3).
The scanning electron microscopic method is a good technique for showing the structure and morphology of solids. The images obtained for the sludge study are similar to those published by El kadiri [24]. The resulting showed non ordered structure with a very heterogeneous distribution of particles.
The X-ray diffraction analysis of the ashes calcified show the existence of Quartz, Calcite, Illite and Analcime in significant amounts (see Fig.5). So the ashes studied can be used as a partial replacement of clinker.

In terms of the characterization of the green-cements designed, Blaine specific area is presented in Tab.5. It should be noted a sensitive increase of the Blaine specific area (over 20%) of cement containing ashes of calcified sludge. However, it is not possible to relate solely the increase in specific surface area to the ashes content incorporated in different cements.

Table 5: Blaine specific area of developed green-cements.

Designation	EC0	EC5	EC10	EC15	EC20
Specific area cm^2/g	3636	4497	4401	4379	4368

The chemical analyses of components of the green-cements were undertaken by X-ray fluorescence spectrometry using equipment of type OXFORD MDX-1000. In parallel, analyses of green-cements developed were also realized. The results are given respectively in Tab.6 and Tab.7.

From Tab.6, we see that ashes resulting from the calcinations of sludge may have a composition close to that of a clinker. Nevertheless, the addition of these ashes in the raw meal for the manufacturing of cement would certainly have required an additional source of lime. The analysis realized on the mixes (Tab.7) confirms this analyses.

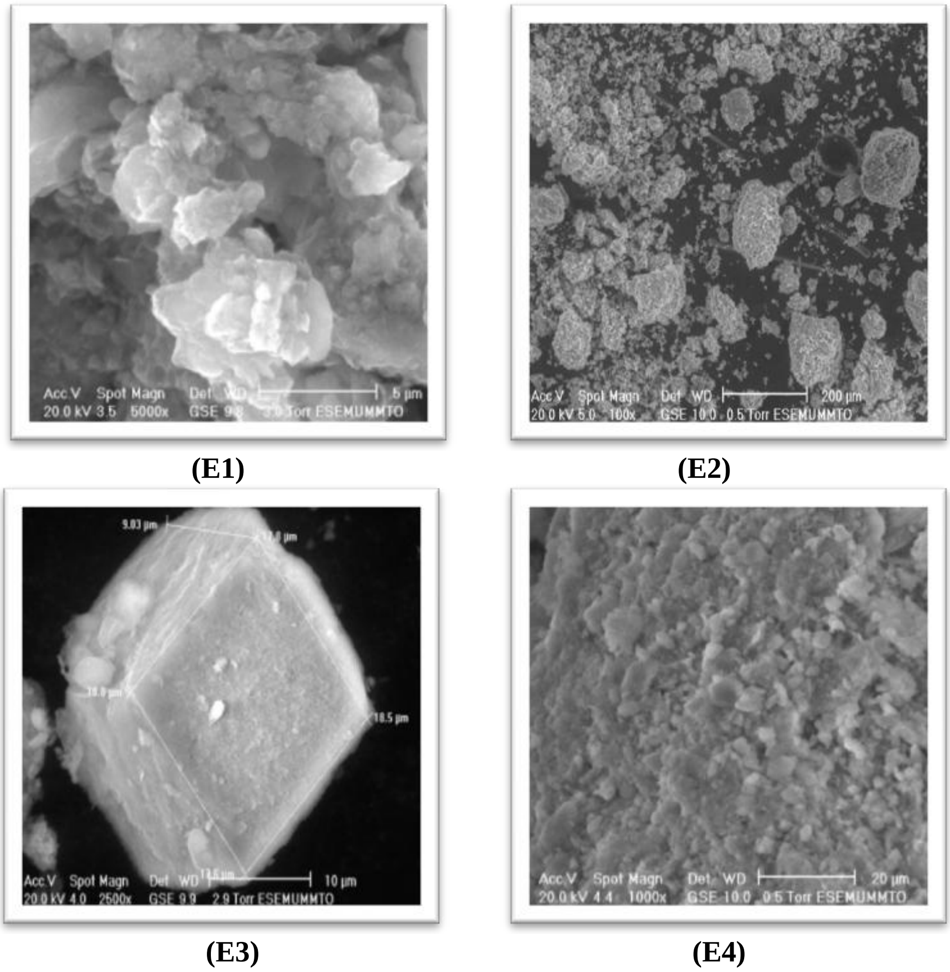

Figure 4: ESEM photograph from E (E1, magnification 500 x; E2, magnification 2500 x; E3, magnification 5000 x; E4, magnification 1000 x) granular sludge.

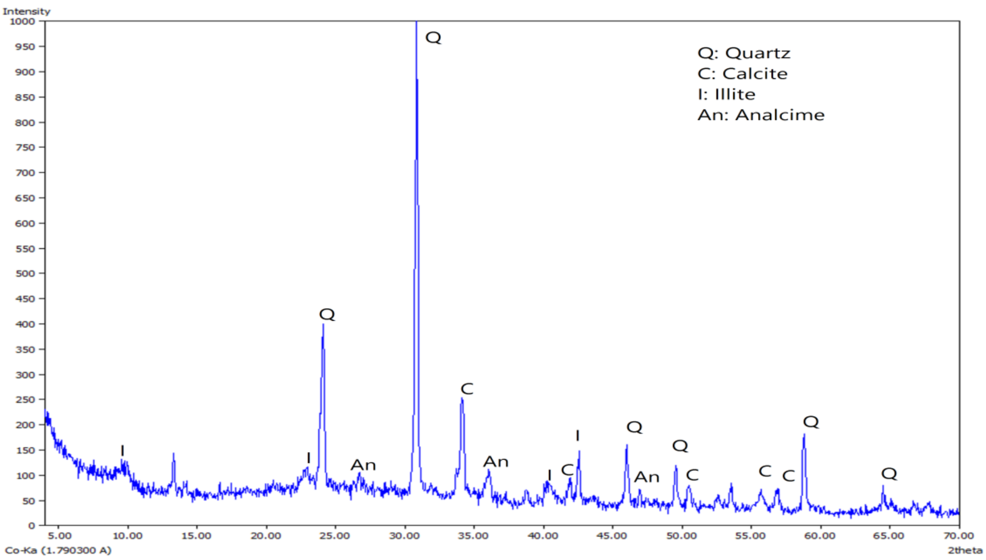

Figure 5: X-ray diffractogram of the calcinated sludge (+550 ° C for 4 hours).

Table 6: Mineralogical composition of clinker, gypsum and ashes.

Component in (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3
Clinker	21.57	5.47	4.02	65.02	0.60	0.123	1.182	1.47
Gypsum	3.70	0.82	0.00	28.08	0.00	0.309	0.179	35.90
Ashes	23.87	7.40	6.36	58.36	2.77	1.35	1.50	0.66

Table7: Mineralogical composition of EC0, EC_5, EC_{10}, EC_{15} and EC_{20}.

Components in (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	PAF
EC0	22.66	5.07	3.77	61.54	1.74	0.164	0.938	2.58	1.61
EC5	23.34	5.41	3.79	59.86	1.83	0.167	0.969	2.58	2.94
EC10	23.78	5.69	3.82	58.13	1.89	0.173	0.988	2.57	4.37
EC15	24.82	6.09	3.90	57.23	1.99	0.186	1.027	2.62	5.31
EC20	25.38	6.40	3.95	55.77	2.07	0.191	1.051	2.52	6.58

To assess the mechanical performances of the new green-cements developed, for each cement type 9 prismatic specimens made of mortar as explained in the first section of this paper are made. At different issues (2 days, 7 days and 28 days) tests in compression and in flexion were performed. The tests were undertaken according to standard EN 196-1. The results obtained are shown in Tab.8.

Table 8: Compressive strength and bending tensile strength of mortars.

	Compressive strength					**Bending tensile strength**				
	2 days	7 days	28 days	f_{c2}/f_{c7}	f_{c7}/f_{c28}	2 days	7 days	28 days	f_{t2}/f_{t7}	f_{t7}/f_{t28}
MT 0%	17.17	30.52	41.40	0.56	0.73	4.37	5.85	6.93	0.74	0.84
MB 5%	21.10	38.60	52.38	0.54	0.73	4.47	6.98	8.32	0.64	0.83
MB 10%	22.20	41.29	51.73	0.53	0.79	4.55	6.77	8.38	0.67	0.80
MB 15%	19.06	38.84	53.73	0.49	0.72	4.35	6.59	7.48	0.66	0.88
MB 20%	16.72	34.64	50.9	0.48	0.68	3.98	6.13	7.42	0.65	0.82

The mechanical results presented in Fig.6 and 7 show that the green-cements used make it possible to develop strengths at the early age (7days) and higher than the strength measured on samples including the standard cement (MT).

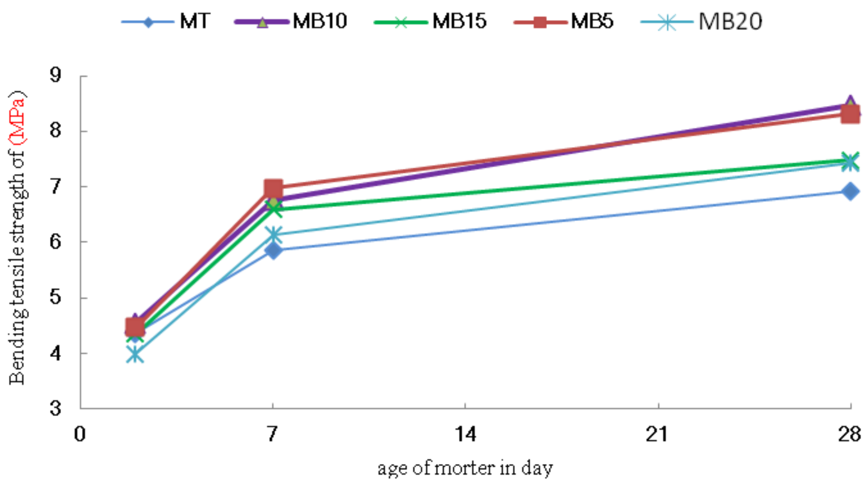

Figure 6: Evolution of the bending tensile strength.

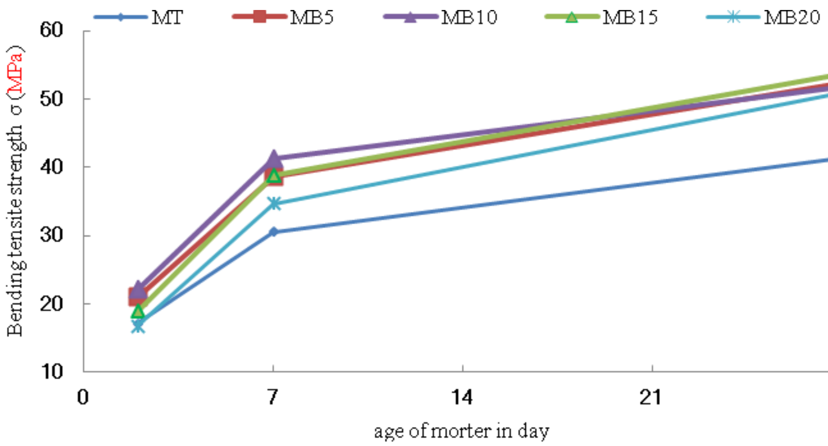

Figure 7: Evolution of compressive strength.

This increase in strength can be attributed, in regard of the measured parameters, to the specific surface developed by the green-cements. The high specific surface area developed by the green-cements (see Tab.5) probably allowed a more important reactivity, hence, high speed of formation of hydrates silicate calcium (H-S-C) gel. The high specific area of the green-cements could predict also finer grain size distribution of the green cement. This later fact could induce an increase of the strength by increasing the compactness of developed mortars.

Conclusion:

In this study, a valuation approach of WWTPs sludge, taken in the district of Sidi Bel Abbes (west of Algeria), in the cement industry has been proposed. A detailed characterization of the sludge and the ashes issued from the heat treatment of the sludge, are performed. This first step has allowed comparing the physical as the chemical characteristics of the studied sludge to the results published in other countries. From this comparative study, it appears that the sludge studied is comparable in terms of physical as chemical characteristics.
Moreover, the chemical and mineralogical analyzes of the induced ashes, have allowed detecting elements comparable to those present in a clinker. Hence, in this work a substitution of the clinker by the ashes up to 20% is tested.
From a point of view of clinker crushing, the addition of ashes sludge induced an increase in Blaine surface. This results needs to be explored in a complementary study.
In terms of mechanical performances of samples made of standard as green cements developed, it appears from this study that the compressive strengths obtained at different curing times, for mortars including the green-cements are higher than the measured values on specimens containing standard cement. It is to note that after 28 days of curing, the resistances of samples made with green-cements exceed 50 MPa. The same trend is observed with specimens tested in bending tensile strength.
These results are more than encouraging for better management of sludge from Algerian plants in the field of cement industry.

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