Valorization of local kaolin in sustainable concrete and on the environment through their exploitation deposit

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Abstract. *The exploitation of clays in the cement sector creates a great influence on the geological monuments as well as on the general geological environment. In this context, this article aims to valorize kaolin from southwestern Algeria in sustainable concrete and to exploit their deposit site as a landfill.*
In order to obtain metakaolin, this kaolin is subjected to a thermal transformation controlled by an apparatus designed to test the ecological efficiency of this material. Subsequently, a mass substitution of 10% of cement with metakaolin in concrete was made for the study the performance of this new concrete.

Key words: Kaolin; Metakaolin; Environment, CO_2 gas; landfill site; Durability

1. Introduction

Cement is a basic component of concrete and mortar used for building and civil engineering construction sectors. Therefore concrete (i.e. cement) is one of the World's most significant manufactured materials. Since it is an essential element in construction materials, understanding the environmental implications of cement manufacturing are becoming increasingly important.
The cement industry is one of the largest carbon emitting industrial sectors in the world [1]. This emissions reached in 2016 of 1.46±0.19 $GtCO_2$ [2]. Fuel combustion emissions of CO_2 are of approximately in total, 8% of global CO_2 emissions [3][4][2]. Approximately 50% emissions of CO_2 are directly emitted from the calcination process (decarbonation of limestone), 40% from fuel combustion in a rotary kiln, and 10% are indirect emissions accounted for quarrying and transportation of products [5][6]. For the production of cement SO_3 and NOx are released in addition to CO_2, which is source of the greenhouse effect and acid rain [7][8].
The cement industry has made significant progress in reducing CO_2 emissions by using of supplementary cementitious materials (SCM) in structural concrete [9][10][11][12].

Low-temperature calcined kaolins, or metakaolins, have very high pozzolanic characteristics, making them excellent supplementary cementitious materials (SCM) for cement-based mortars and concretes [13][14].

The Metakaolin ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) is prepared by dehydroxilation of kaolin clay in the temperature range of 450–850 °C [15], [9].

The environment is dynamic. It undergoes modifications through several processes, including the exploitation of natural mineral deposits in construction [16].

Exploitation of mineral resources has assumed prime importance in several developing countries including Algeria.

Indeed, the extractive industry, through the application of different techniques and technologies, has always been a source of damage to the environment. Such exploitation has a massive and largely negative impact on the reliefs [17].

Also, the development of technology and population growth leads to significant generation of solid waste [18] and the continual increase in the amount of household waste and toxic industrial waste. A modern landfill is an engineered method for depositing waste in specially constructed and protected cells on the land surface or in excavations in the land surface. But the characters of the proper choice of landfill site are very difficult. These criteria encompass environmental conditions, accessibility, geological and hydro-geological conditions, ecological and societal effects.

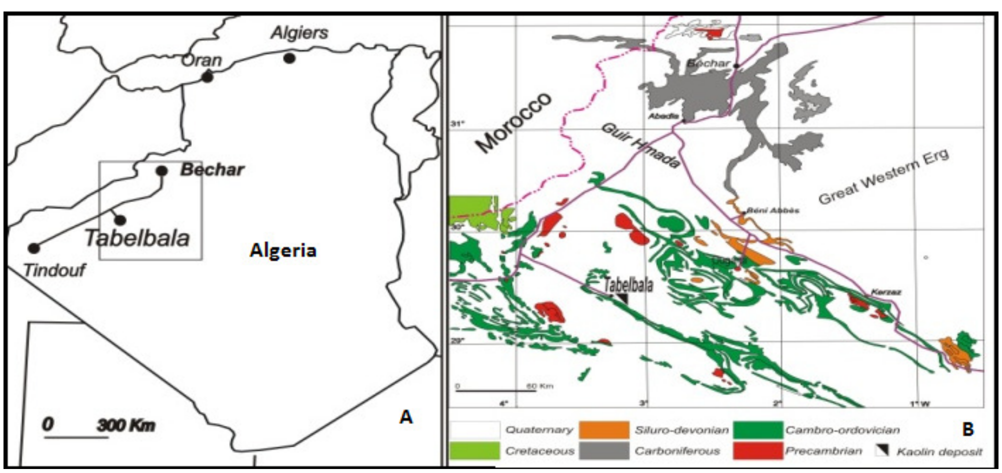
This article articulates on two research shutters that are:

The first shutter is the study of the ecological efficiency of local metakaolin, and its effect on the durability of concrete by substitution of 10% of Ordinary Portland cement (OPC).

In the second shutter, we contribute to the valorization by geotechnical characterization to exploit the site of footprint deposit of kaolin to landfill site.

Kaolinic clays are available in Algeria, including his South- Western [19], [20].

The kaolin targeted by this study is located in the South East of new constructions of Tabelbala at 314 km south of Bechar in Algeria (fig.1.A). Geologically, the deposit belongs to the Silurian floor Ougarta Mountains [21] (fig.1.B).



(A): localization of Tablebala city (B): Geological sketch map of the Ougarta Range [21]

Fig.1. Location and illustration of the Tabelbala kaolin deposit

For many centuries, kaolinic clays have been exploited in the Tabelbala (Algeria) as a cement or waterproof cover on the roofs. They are associated with lower Paleozoic sandstones [22].

This kaolin is in the form of lentils of 3 to 5 km in length, estimated at 500 thousand tons, and is located more precisely in the village of Mekhlouf, south of the city of Tabelbala, which constitutes a prodigious wealth [19].

Our principal objective of this research is the used the means, equipments, and materials simple locally available.

Remark: To lighten the writing of the article, metakaolin is sometimes replaced by the symbol MK.

2. Materials and Methods

2.1. Mineral addition

2.1.1. Sampling

The clay mineral kaolinite is formed by the breakdown of feldspar by the action of water and carbon dioxide. Kaolin samples were taken in the open-air after stripping a thin slender layer of waste rock composed of scree.

2.1.2. Geotechnical characteristics

The collected samples were subjected to laboratory tests for to define of essentials geotechnical parameters. These parameters, concerns namely grain size distribution by Hydrometer analysis, water content, Atterberg limits, solid grain density, methylene blue value, and volumetric mass wet and dry determine according to standards edited by AFNOR (French Standards Association).

Using the correlation formulas and the grading curve must , porosity, void ratio, median grain size, percentage of the clay fraction, activity value and the permeability have been determined of this type of clay.

The activity and permeability are two properties particularly important in environmental protection for the determination of water and contamination retention capability of soils.

By relationship (1), Skempton (1953) defined activity as the ratio of plasticity index to < 0.002 mm clay fraction.

$$\mathbf{S} = \frac{\boldsymbol{I_P}}{\boldsymbol{C}\,[\%]} \qquad (1)$$

Respectively *S*, *Ip* and *C* are activity values, plasticity index and clay fraction percentage. The coefficient of permeability is calculated from the Berg relationship by formula (2).

$$\mathbf{k} = \mathbf{8.4x10^{-2}(d)^2\Phi^{5.1}} \qquad (2)$$

Where: *k*, *Φ* and d are permeability (mD), Porosity and fraction median grain size (microns) respectively.

The average values of the geotechnical parameters obtained from the tests carried out on four samples of kaolin are mentioned in table 1.

Table1. Results of geotechnical parameters of kaolin samples

Parameters	Average values
Water content (%)	0,75
Volumetric weight γ(t/m^3)	1,98
Dry volumetric weight γ_d (t/m^3)	1,96
Clay fraction C [%]	≈ 51
Plasticity index I_P	24,6
Density of the solid particles ρ_p (t/m^3)	2,66
Porosity fraction (Φ)	0,26
Void ratio	0,35
median grain size d (mm)	0,0018
Skempton's Activity value S	≈ 0,48
Permeability k (mD)	≈2,82E-4
Methylene Blue Value : MBV (mg/g)	2,17

The particle size distribution of this kaolin determined by Hydrometer analysis can be represented graphically in fig. 2.

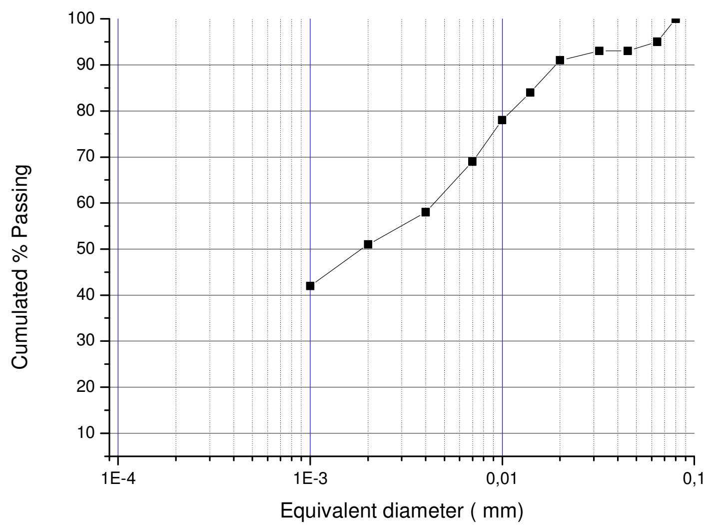


Fig.2. Particle size distribution of Kaolin

2.1.3. Mechanical treatment the kaolin and metakaolin samples

The mechanical treatment, comprising three successive processes of crishing: by jaws, cylinders and by discs in order to obtain fine particles having elements less than 100µm. This material is ground to a required finesse beyond of 900m^2/kg.

2.1.4. Thermal treatment of the kaolin sample (calcination)

In order to produce a metakaolin nearly complete dehydroxilization must be reached without overheating, i.e., thoroughly roasted but not burnt.

The valorization of the environmental efficiency of metakaolin requires control of the quantity of gas emitted during the calcination of kaolin. For this purpose, an apparatus composed of a sealed muffle furnace associated by its chimney with a Bernard calcimeter by means of a flexible rubber hose (fig. 3) was created. The muffle furnace is for calcining kaolin and the calcimeter is for measuring the amount of gas emitted during calcination of kaolin. The displacement of the colored liquid in the tube graduated of calcimeter, indicates the quantity of gas emitted and is equal to the difference of the graduations before and after calcination of kaolin.

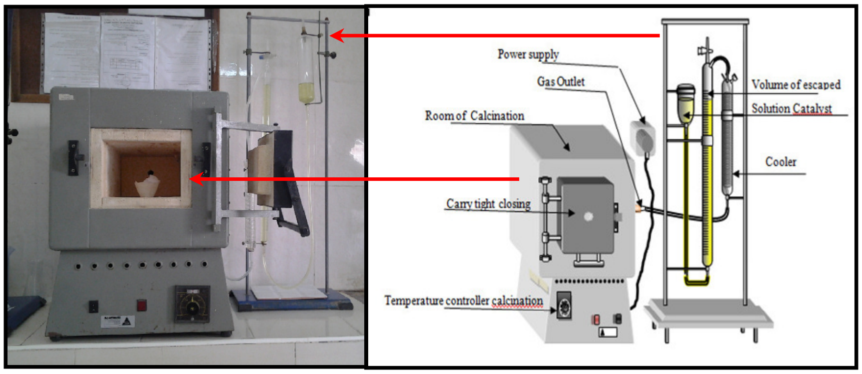


Fig.3. Gas measuring device (muffle furnace – Calcimeter)

The metakaolin studied, is obtained by calcination of the kaolin at temperatures between 450 and 760°C for about five (05) hours, according to the thermal cycle indicated in fig. 4.

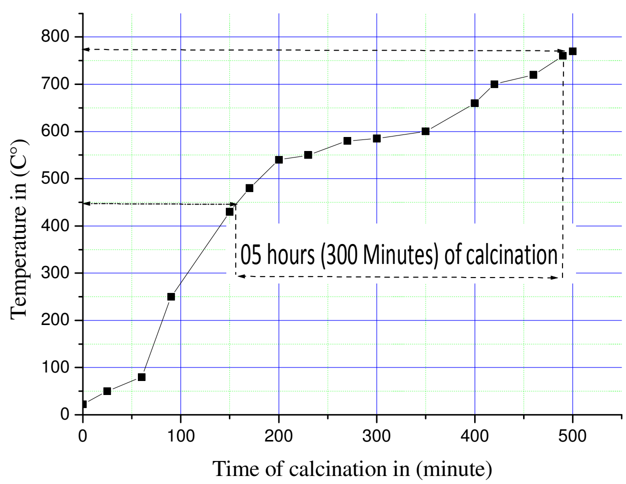


Fig.4. Cycle thermal processing of the Tabelbala kaolin

2.1.5. Identification chemical of metakaolin

The chemical analysis is carried out according to methods of the standard EN 196-2 [23]. The results of the chemical analysis of MK are given in Table 2.

Table2. Results of chemical composition of metakaolin sample

Chemical Composition,%	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	CaO	SO_3	MgO	TiO_2	Loss on ignition
MK	49,38	36,76	6,68	0,50	1,89	0,25	0,88	0,43	0,79	2,73

The chemical test results of the MK specimen were compared with the ASTM C618 [24] requirements, as shown in Table 3.

Table3. Result of comparison between pozzolan chemical properties and ASTM requirements

Test	MK	ASTM C618[24]			
		Natural pozzolan N Class	Fly ash		Silica fume
			F Class	C Class	
Sum of Iron Oxide (Fe_2O_3), Aluminum Oxide (Al_2O_3), and Silicon Dioxide (SiO_2),%	92,82	≥ 70	≥70	≥ 50	-
Sulfur Trioxide (SO_3),%	0,88	≤4	≤5	≤5	-
moisture content	small	≤3	≤3	≤3	-
Loss on ignition (%)	2,73	≤10	≤6	≤6	≤6
Silicon Dioxide (SiO_2),%	49.38	-	-	-	≥ 85

2.1.6. Mineralogical Identification of metakaolin

Mineralogical analysis of this metakaolin was carried out by X-ray diffraction using standard equipment INEL CPS 120 and with the use of software X PERT DATED COLLECTOR whose results are shown in Table 4.

Table4. Mineralogical content of metakolin

Elements	Quartz	Kaolinite	Muscovite	Ferruginous minerals	Albite
Percent by Weight	50,00	19,00	19,50	6,50	5,00

2.1.7. Morphology of metakaolin

The morphology of MK is obtained by (SEM-SE) scanning electron microscope using secondary electrons (fig. 5).

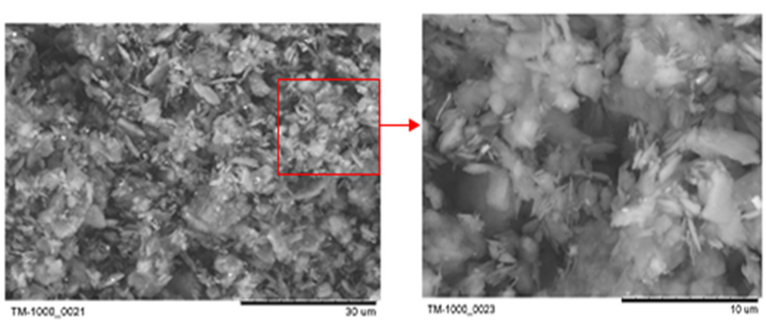


Fig.5. SEM-SE Morphology of MK: A low magnification and higher magnification.

2.1.8. Physical identification

Physical identification includes: pozzolan activity index (AI) realized according to the modality of the ASTM C311 standard [25] , the density was measured by hydrostatic

weighing after saturation of the sample under vacuum and specific surface measurement. The results found are shown in Table 5.
For assessed the pozzolan activity index, The materials used are the standard sand CEN conform EN 196-1 [26], cement (CEM I 52.5 N) and drinking water.
The specific surfaces (S) of metakaolin powder and cement are determined by the BET (model Brunauer, Emmett and Teller BET) method and Blaine method respectively.

Table5. Results of the principal physical identification of cement and metakaolin

	Density (g/cm^3)	S (m^2/g)	Activity index (AI)		
			07 days	28 days	90 days
Cement	3.14	0.3818	1.00	1.00	1.00
Metakaolin	2.7	16	0.79	1.00	1.09

2.2. Concrete mix design

For economic reasons, all components (aggregates, kaolin, cement, and water, additive) of concretes are local materials. The metakaolin obtained from local kaolin is used to replace part of the CEM I 42.5 cement

2.3. Concretes formulations

Two concrete compositions were made, one without MK (C1), the other MK replace 10% of the weight of cement (C2), and with superplasticizer.
For a performance comparison between C1 and C2 concretes, we selected a constant slump of Abrams cone equal to 9cm. Metakaolin consumes a higher quantity of superplasticizer compared to the cement, this is the reason that the rates of water/cement (W/C), the quantity of water and superplasticizer are different between the two formulations. The quantity of binder (cement and MK) and quantity inert components (sand and gravel) have remained constants.
The choice of 10% metakaolin as the level of cement substitute is based on the results of other researchers. In research of Barbhuiya and its collaborators, the 10% is the optimal rate comparatively 0%, 5%, 10% and 15% of metakaolin for the evaluation of compressive strength, absorption capacity and carbonation of concrete[27].The introduced proportions are given in table 6.

Table 6. Composition of concrete with and without metakaolin (kg/ m3)

Designations	Cement CEM I 42,5	Metakaolin	Aggregates			Superplasticizer (ADVA Flow 390)	Mixing water
			Sand 0/5	Gravel 3/8	Gravel 8/15		
C1	440	0	530	300	875	C1	440
C2	400	40	530	300	875	C2	400

2.4. Performances tests

2.4.1. **Dynamic Young's Module** [28]

The phase velocities of the longitudinal wave and the transverse waves measured by ultrasound (in the case of aggregates) are linked to the elastic modulus and to the Poisson's ratio by the relation (3).

The ultrasonic wave propagation velocity method was realized according to standard NF EN 12504-4 [29] of 70 × 70 × 280 mm^3 concrete specimens.

$$V_l = \sqrt{\frac{E_{dy}(1-\vartheta)}{\rho(1+\vartheta)(1-2\vartheta)}} \quad (3)$$

Where:

ϑ: is the Poisson's ratio of the material,

E_{dy}: is the dynamic Young's modulus of the material,

ρ: is the density, known and measured independently

2.4.2. Compressive strengths

Compressive strength tests on cured cubic concrete specimen of 28 and 90 days ages were performed using a compression testing machine accordance with standard NF P 18-406.

2.4.3. Estimation of the Capillary Water Absorption Coefficient

According to ASTM C1585 [30], the capillary water absorption coefficient is the gradient of the straight fine obtained by plotting the cumulative mass of water absorbed per unit area against the square root of time t obtained from this first stage according to the following equation (4):

$$\mathbf{A_w} = \frac{\Delta \boldsymbol{M}}{\boldsymbol{A}\sqrt{\boldsymbol{t}}} \quad (4)$$

Where A_w ($mg/cm^2s^{1/2}$) is the water absorption coefficient, $\boldsymbol{A}$ (cm^2) is the surface area of the cross section of the specimen and ΔM (mg) is the mass of the absorbed water as shown in Fig.6.

This coefficient is calculated at 24 hours that is to say between 24h-0h and 48h-24h on cubic specimens of section 10x10cm^2.

Fig.6. Water absorption test on concrete cubes

2.4.4. Penetration depth of chloride ions in calorimetrically hardened concretes [31]

The test described here makes it possible to determine the depth of penetration of the chloride ions in a material, from the vaporization of a reagent, the silver nitrate $AgNO_3$, and optionally a developer, potassium dichromate K_2CrO_4.
The determination of the chloride penetration depth X_d is also necessary for the calculation of the apparent diffusion coefficient D_{app} expressed in $m^2.s^{-1}$ (Eq. (5)) from a non-stationary electric field migration test.

$$D_{app} = 1{,}189\frac{10^{-11}\left(X_d - 1{,}189.X_d{}^{0{,}589}\right)}{t} \qquad (5)$$

Where t is the test duration, [hours];

2.4.5. Sulphate resistance

The sulphate resistances are determined from the concrete specimens after storage for 28 days (zero time), then a series of these specimens is immersed in the sodium sulphate solution Na_2SO_4 with 5% concentration and others are stored in the water. To evaluate the durability of the concretes with respect to sulphate attack, we determined the compressive strength as a function of the immersion time in the sulphate solution. For all tests, the samples are preserved at 20°C.

3. Results and Discussion

3.1. Thermal treatment of the kaolin

The values, measured by the displacement of the volume in the graduated burette of Bernard's calcimeter (Fig.4), are almost negligible. This testifies that this metakaolin during its production releases only water vapor explained by the following chemical reaction:

$$Al_2Si_2O_5(OH)_4 \rightarrow Al_2O_3\,2SiO_2 + 2H_2O\uparrow$$

Unlike metakaolin, the production of Ordinary Portland Cement requires a strong heat creating a harmful effect on the environment.

3.2. Chemical and mineralogical results

The chemical results of the metakaolin obtained are almost similar to those of the fly ash, but did not meet the requirement of 85% silicon dioxide for the silica fumes (see Table 3 below).
Also, the images obtained by SEM-SE for two levels of magnification, show that the MK consists essentially of agglomerates of particles. These latter are formed a stack of hexagonal plates. The dimensions of the platelets vary from 1 to 10 µm

3.3. Mechanical parameters

For a Poisson's ratio taken $\vartheta = 0.2$ the results are shown in Table 7.

Table7. Average values of mechanical parameters

Formula	Bulk Density [kg/m³]	Compression Strength [MPa]			Modulus of elasticity [MPa]
	14 Days	14 Days	28 Days	90 Days	14 Days
C1	2349	38	45	48	32637
C2	2422	43	50	65	41840

These results shows that the substitution of cement with metakaolin leads to an improvement of the mechanical strengths at 14, 28 and 90 days, this increase is very remarkable and is consistent with that of the literature [32][33][34][35][36][37].

3.4. Capillarity test (capillary absorption)

The capillary water absorption coefficient is one of the most important features of durability the concrete because it governs the liquid moisture movement into it and expresses the rate of absorption of water due to capillary forces in this building material. The average results obtained by the capillary absorption test as well as those of absorption of the two (02) types of concretes at 20°C are given in the histogram of fig 7.

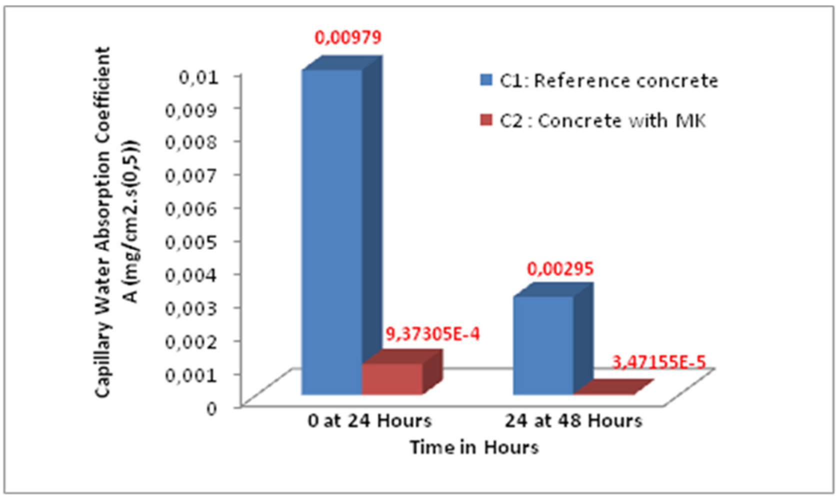


Fig.7. Evolution in 24 hours of water absorption coefficient Aw for the two samples concretes

In light of the results obtained, it is clear that the water absorption coefficient by capillarity is rapidly increased after the first 24hours. But, it is gradually decreasing for the reference concrete and stabilized for the concrete with metakaolin. These results explain that metakaolin reduced the pores of the concrete matrix and led to low capillary absorption compared to the reference concrete. This discovery was developed in the research of Wojciech Kubissa and his collaborators [38].

3.5. Penetration of chloride ions

The different diffusion coefficients calculated from the formula (5) are given in Table 8.

Table8. Results of the penetration of chloride ions in hardened concretes

Formula	X_d (mm)	D_{app} [$m^2.s^{-1}$]
C1- reference concrete	8	$3.34.10^{-12}$
C2- concrete with metakaolin	3	$0.48.10^{-12}$
	No color	Negligible

The diffusion of the chlorides in the control concrete and the metakaolin concrete are illustrated in fig.8A and fig.8B respectively.

Fig.8. Diffusion of chlorides in control concrete (A) and concrete with metakaolin (B)

These experimental results reveal that the diffusion coefficient in metakaolin concrete is very low to negligible (fig. 9B) compared in the reference concrete (fig. 9A) because of its very dense porous structure. This shows that this concrete has not been degraded by penetration of chloride ions over time. The diffusion coefficient of concrete C2 is less than 2 x 10^{-12} m^2/ s attests a very good resistance to chloride penetration [38].

3.6. Sulphate resistance of concretes

After the specified days, the samples were immersed in 5% sodium sulphate solution (Na_2SO_4) for 24 months. The results of the variation in compressive strength for the two types of concrete immersed for 4 months, 8 months and 12 months in his solution prepared are shown in (fig 9).

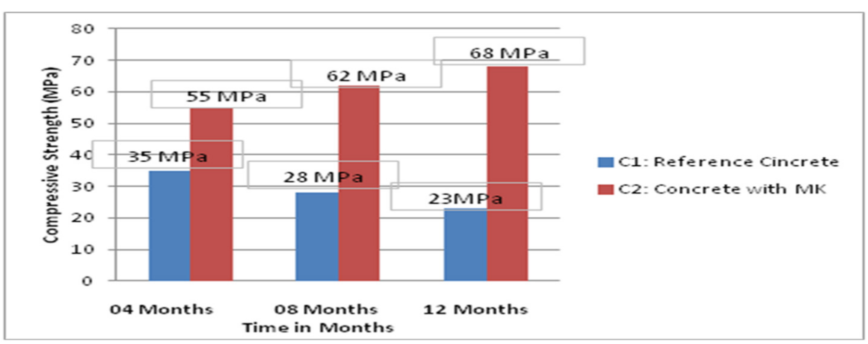


Fig.9. Variation of compressive strength of concretes immersed in sulfate solutions as a function of shelf life

Metakaolin addition proved to be beneficial in improving the resistance of concrete to sulphate attack. It can be seen that the compressive strength of the reference concrete was inversely proportional to the conservation time them in the sulfated solution and on the contrary, concrete with metakaolin have the slightly increased resistances, this is due to the dense matrix (cement / metakaolin).
The action of sulfates can also lead to a loss of resistance and a loss of mass of the concrete ordinary (reference) in surface. These effects are explained by author Saida BOUALLEG [39], by the fact that they are due to the alteration of binding properties of certain hydrates.

3.7. Landfill Site

The impermeability of the geological formation is highly recommended for the choice of the sites of the landfills and this to prevent any possible infiltration of pollutants which may jeopardize the water resources and especially groundwater as it is difficult to know the formations of polluting flows generated by the anaerobic decomposition of waste.
Knowledge of the principal clay mineral (e.g. montmorillonite, illite, and kaolinite) property is particularly important in environmental protection for the determination of water and contamination retention capability. Skempton's Activity value (S) [40], is especially useful for evaluating this behavior. Skempton's Activity is not a consistency parameter, but affects the values of consistency limits.
Skempton activity values found (fig.10) show that Tabelbala kaolin is inactive clay.

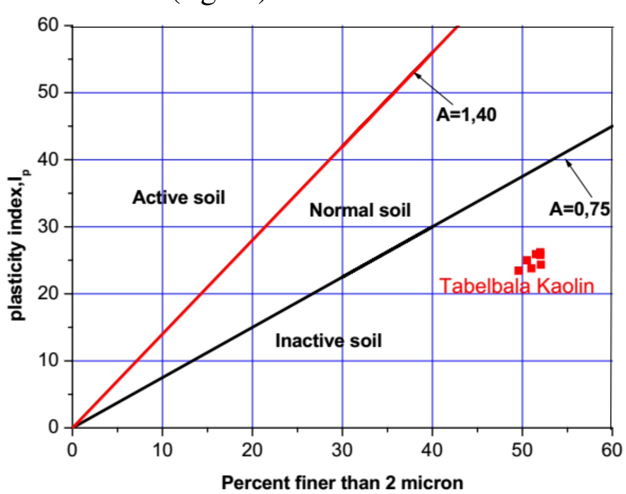


Fig.10. Classification of the Tabelbala kaolin according to activity

According to the Unified Soil Classification System (USCS) and using the Casagrandes plasticity table, this kaolin is inorganic clay of moderate plasticity.
Because of their impermeability, this kaolin plays an important role in the circulation and accumulation of various fluids (e.g. water, oil, gas); this finding is approved by its low coefficient of permeability found.

4. Conclusions

The compositional analyses of Tabelbala kaolin deposit have been carried out in this study. Comparisons have been made with the works of other authors and inferences also drawn to confirm the results of the analyses and economic viability of the deposit. The analysis results show that kaolin of Tabelbala could be a suitable raw material in the production of addition and / or substitution of Portland cement.

Ecologically, unlike the cement manufacturing method, the heat treatment of kaolin from the Tabelbala region confirmed that there is no release of greenhouse gas emissions during the production of metakaolin and releases only the water vapor.

Economically, the production of metakaolin requires a single deposit (kaolin) compared to cement which requires several (limestone, clay, gypsum...).

In terms of performances, the substitution of 10% of the cement by the metakaolin allows a significant improvement of the performances of the concrete (dynamic Young's modulus, Compressive strengths, capillary absorption, penetration of chloride ions and sulphat resistance).

In addition, the geological formation in place of the kaolin exploitation site is of an impermeable and inactive nature which leads us to an economic choice of this site for the realization of a landfill.

At the completion of the operation of the exploitation of material deposit, a sufficient thickness of the kaolin layer must be compacted superficially about 20 to 25 cm to ensure good sealing and good support of waste depositing.

A waterproof membrane is then placed over the exposed soil to prevent leachate from soaking into the surrounding soil and groundwater.

The kaolin is spread across the membrane to form another protective layer.

In the end, local metakaolin is both a less polluting cementitious material, high-performance in new concrete, economical, and ecologically efficient.

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