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Use of Phosphate Waste as a Building Material

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1. Introduction

A phosphate mining waste, called Feral is produced during the processing of a phosphate rich alumina (25wt% P_2O_5 , 27wt% Al_2O_3 , 9.53 wt% Fe_2O_3) which makes up the Lam-Lam deposit in western Senegal (Fig. 1). Lam-Lam is one of the few aluminium phosphate deposits in the world. These unweathered Al-phosphates are mined by the Société Sénégalaise des Phosphates de Taïba (SSPT) near the village of Lam Lam, northwest of Thiès. These phosphates occur as 7 m thick layers under a thick iron crust. Proven reserves of this deposit are 4 million tones of marketable product with an average grade of 33% P_2O_5 . Only 1.5 million tones of these reserves have an overburden of less than 24 m (McClellan and Notholt 1986).

During processing, 30% of the phosphates are disposed of as waste (0/5mm in size). The waste is called Feral due to its high iron and aluminum oxide content: 10 and 27 wt %; respectively. Lam lam deposit is only a few kilometres flying distance from the seashore.

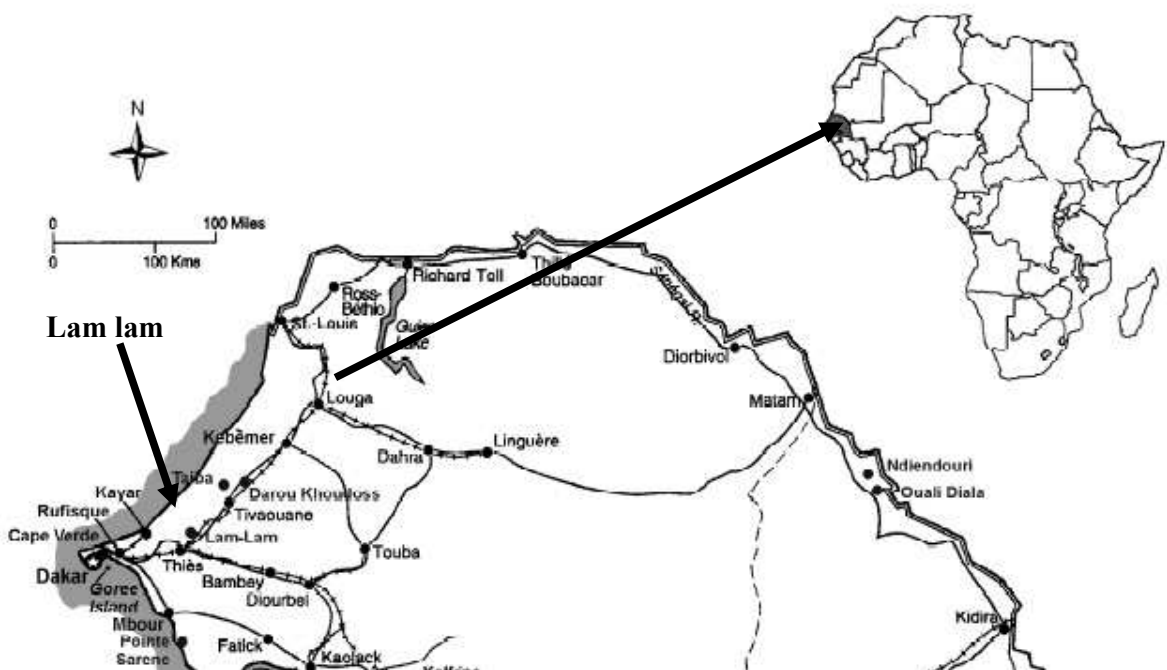


Fig. 1. Map of the African continent showing the location of Senegal and the Lam-Lam phosphate deposit.

It is anticipated that approximately 15 million tonnes of Feral will be produced in the coming years. This is a significant amount of waste material. Unfortunately Senegal, a developing country in West Africa, does not have the money or technology to recycle these wastes. Thus they languish in lakes and ponds where they have the potential to impact the environment in a negative fashion. In this note, we explore the possibility of using it as a building material and in road construction.

Table 1 gives the chemical composition of Feral in weight percent. The major oxides are: Al_2O_3 , P_2O_5 , SiO_2 and Fe_2O_3 . The position of Feral in the double triangle diagram shows that it's possible by adding caustic solution to form geopolymer and AlPO_4 zeolite (Dyer, 1999).

SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	TiO_2	MnO	P_2O_5	BaO	SrO	LI
12.5	6.76	27.0	9.53	0.08	0.13	1.27	2.01	0.03	24.9	0.09	0.42	15.28

Table 1. Chemical composition of Feral (wt %)

Figure 2 shows the positions of the Feral deposit both on the SiO_2 , Na_2O and Al_2O_3 triangle and the P_2O_5 , CaO and Al_2O_3 triangle.

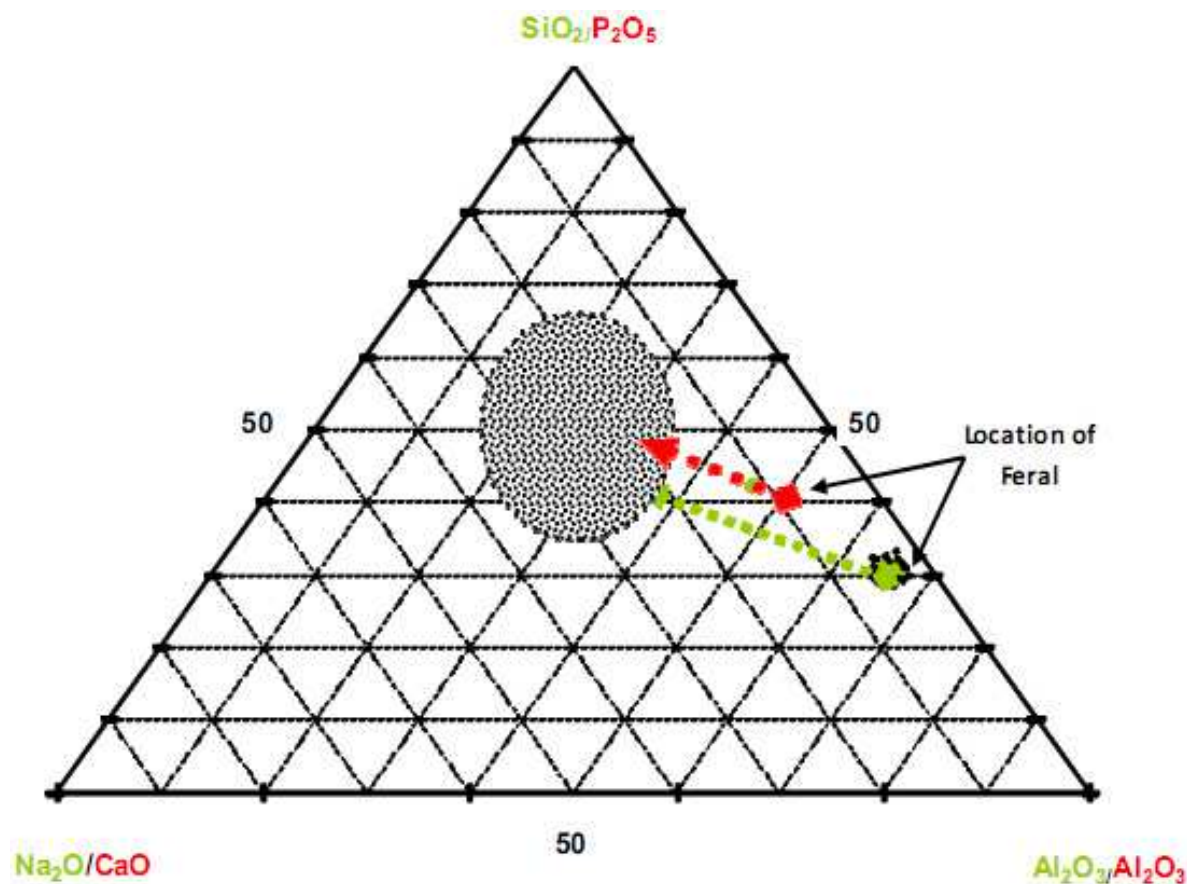


Fig. 2. Positions of the Lam-Lam phosphate deposit on the SiO_2 , Na_2O and Al_2O_3 and P_2O_5 , CaO and Al_2O_3 triangles and the location of the zeolite domain

2. Available raw materials

Varieties of clay, highly weathered rock (laterite, tuff) and mining waste (aluminum phosphate, calcium phosphate, phosphogypsum) are materials available in Senegal for making bricks.

The substratum of the Senegalese territory is made up of two major geological domains: the the shallow-dipping Upper Cretaceous to Quaternary sediments in most of the central and western parts of Senegal, which occupies more than 75% of the territory, and the Precambrian basement, and in the east by the Palaeoproterozoic volcano-sedimentary sequences of the Kedougou- Kenieba inlier.

The Precambrian basement formations are constituted at the west by the Mauritanides range bordering the eastern part of the Sedimentary Basin and in the east by the Palaeoproterozoic volcano-sedimentary sequences of the Kedougou- Kenieba inlier. The Kedougou-Kenieba inlier is limited to the west by the Mauritanides chain and on all other sides by the Upper Proterozoic and Cambrian sediments of the Basin of Taoudenni. The Kedougou-Kenieba inlier is interpreted as an accretion of north-easterly trending Birimian age volcanic terrains. Geological studies suggest that mineralisation in the prospective Sabodala volcano sedimentary belt and the Senegal-Malian shear zone is associated with an altered and sulphidised gabbro, which has intruded along the main structure, and a typical shear zone, hosted, where a structure has developed at the contact between a package of volcanoclastics and sediments. A lapilli tuff acts as a prominent marker horizon in the hanging wall of mineralisation.

The inlier is divided into three main stratigraphic units from west to east: the Mako Supergroup, the Diale Supergroup and the Daléma Supergroup.

- The Mako supergroup include basalt flows; often carbonate alterations and minor volcanoclastic intercalations, magnesium basalt or komatiites, ultramafic sub-volcanic intrusions (pyroxenites) and numerous massive biotite and amphibole granitoids.
- The Diale Supergroup, located between the Mako Supergroup and the western edge of the Saraya granite consist of shale, greywacke, quartzite and volcanodétritic rocks.
- The Dalema Supergroup, is composed of volcano-sedimentary schist and grauwacke rocks.

In addition, there are large marble and other ornamental rocks deposits, but also non metallic indices and deposits of barytes, kaolin, asbestos etc.

The Senegal Basin occupies the central part of the Northwest African Coastal Basin, which extends from the Reguibat ridge at the north end of the Guinean fault.

Most of the outcrops of the basin are composed of recent sandy covers. The Secondary formations include Palaeocene zoogenic limestone exploited at Bandia and Pout by cement plants and aggregates producers. They include also Maestrichian sands, clays and sandstones.

Tertiary formations hold into the Eocene compartment, significant resources of phosphates, limestone, attapulgitite, clay and ceramics, solid fuels, etc. A major part of the basin is covered with superficial Quaternary formations, which in the middle and recent parts are

characterised by fixed red sand dunes, semi-fixed or alive yellow and white dunes. These dunes, often exploited as building materials around urban centres, constitute also important reservoirs of heavy minerals.

3. Procedure

3.1 Identification of Feral

This particular Feral has been characterized using a variety of techniques including chemical and physical analyses. X-ray diffraction was used for mineralogical analyses.

The California bearing ratio (CBR) is a penetration test for evaluation of the mechanical strength of road sub grades and base courses.

The test is performed by measuring the pressure required to penetrate a soil sample with a plunger of standard area. The measured pressure is then divided by the pressure required to achieve an equal penetration on a standard crushed rock material. The CBR test is described in ASTM Standards D1883-05 (for laboratory-prepared samples) and D4429 (for soils in place in field), and AASHTO T193. The CBR test is fully described in BS 1377: Soils for civil engineering purposes: Part 4, Compaction related tests.

The CBR rating was developed for measuring the load-bearing capacity of soils used for building roads. The CBR can also be used for measuring the load-bearing capacity of unimproved airstrips or for soils under paved airstrips. The harder the surface, the higher the CBR rating. A CBR of 3 equates to tilled farmland, a CBR of 4.75 equates to turf or moist clay, while moist sand may have a CBR of 10. High quality crushed rock has a CBR over 80. The standard material for this test is crushed California limestone which has a value of 100.

3.2 Treatment of Feral by cement Portland

Some materials used in road geotechnics have to be treated by binders in order to have their geotechnical characteristics conform to standards.

The aims of these treatments are to improve their geotechnical properties:

- aptitude to compactness;
- decrease of water sensibility;
- increase of strength and load bearing capacity.

The cement used here is a Portland cement fabricated by SOCOCIM-Industries, the first cement plant in Senegal. The composition of the cement used in this study and fabricated by SOCOCIM-Industries is summarized on table 2. The cement have around 1wt% of P₂O₅.

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	P ₂ O ₅	K ₂ O	Na ₂ O	SO ₃	Free CaO
21.8	5.10	3.40	66.18	0.68	0.82	0.33	0.05	0.61	2.04

Table 2. Composition cement fabricated by SOCOCIM-Industries (wt%)

For aggregate used in Senegal for road construction, the CBR must be greater than 80 % for substructure and 30% for sub base (Table 3).

Lateritic aggregate	substructure	sub-base.
CBR after 4days immersion (%)	≥80	≥30

Table 3. Criteria of use of lateritic aggregate in Senegal

Table 4 represents the criteria of use of a soil-cement in Senegal based mainly on the CBR value and the compressive strength.

Soil-cement	substructure	sub-base
CBR after 3days in air and 4days immersion (%)	6-80	≥ 160
CBR after 7days in air (%)	80-120	-
Compressive strength after 3days in air and 4days immersion (bars)	25-5	≥5
Compressive strength after 7days in (bars)	5-10	18-30

Table 4. Criteria of use of a soil cement in Senegal

Cement content used for the treatment of soil are low for cost reasons, they vary generally between 0 and 3% as represented in Table 5.

Improvement of Feral waste					
% of cement	1	1.5	2	2.5	3

Table 5. Cement content (wt %) used to treat Feral

3.3 Treatment of Feral by alkali activation

3.3.1 Mixes

Geopolymers are chains or networks of aluminosilicate mineral molecules linked with covalent bonds. Different geopolymers can be distinguished following their molecular units (Davidovits, 1989; Cioffi et al., 2003):

- (-Si-O-Al-O-) polysialate with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio equal to 2,
- (-Si-O-Al-O-Si-O-) polysialatesiloxo with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4$,
- (-Si-O-Al-O-Si-O-Si-O-) polysialatedisoloxo with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4$.

The aluminosilicate kaolinite reacts with NaOH at 100-150°C and polycondenses into hydrosodalite-based geopolymer ($\text{SiO}_2/\text{Al}_2\text{O}_3=2$). A polysialatesiloxo ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 4$) is obtained from metakaolin and NaOH. These inorganic polymers have a chemical composition somewhat similar to zeolite A ($\text{Na}_{12} [\text{Al}_{12}\text{Si}_{12}\text{O}_{48}] 27\text{H}_2\text{O}$) (Breek, 1974; Dyer, 1988) but exist as amorphous solids, rather than having a crystalline microstructure.

Figure 2 shows the location of Feral in a SiO_2 - Na_2O - Al_2O_3 compositional diagram. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ is equal to 4.3. It suggests that geopolymer can be obtained from this Feral by adding NaOH. Different processes can be proposed. In the first one, Feral is mixed with sodium hydroxide and allowed to react in large heated boiling-water vessels. The water-rich slurries are stirred until geopolymer formation and the completion of the reaction. In the second one, monolithic samples can also be produced, but with a lower water content. In this last case, stoichiometric amounts of 4 to 12M NaOH are mixed with the dry ingredients to form a thick putty-like paste. This paste is then molded and cured at elevated temperatures. Monoliths made in this way are generally very strong and highly insoluble. (Berg et al., 1965; Palomo et al., 1999b; Bao et al., 2004; Grutzeck et al., 2004; Bao et al., 2005, Bao and Grutzeck, 2006). It is this last process which used in this study.

The work reported here is an outgrowth of our previous work (Diop, 2005, 2007, 2008). In this study we point out that this process using the Feral is possible.

3.3.2 Samples

Feral sample were mixed with different alkali concentrations (4, 8 and 12 molar NaOH) to form thick pastes (Table 6). The DTM sodium silicate used in the formulation 11 is composed of silicic acid, sodium salt; sodium silicate which constitute 44.1wt% and water. In the DTM, the ratio $\text{SiO}_2/\text{Na}_2\text{O}$ in weight percent is equal to 2.

Samples	Feral (wt %)	NaOH (wt %)	Cure Temp (°C)	Cure time (days)
1	80	4Molar (20)	120	0.25
2				0.5
3				1
4	80	8Molar (20)	120	0.25
5				0.5
6				1
7	80	12Molar (20)	120	0.25
8				0.5
9				1
10	80	15Molar (20)	120	0.5
11	80	Mix Molar (20)*	120	0.5

*(100g 8Molar NaOH + 250g " DTM " sodium silicate)

Table 6. Formulations studied for bricks manufacturing

The entire eleven samples tested are composed of 80%wt Feral and 20% of solution. After vigorous hand-mixing, the treated Feral was statically compacted in a 2.5cm diameter cylinder. The compaction was carried out by a hand-operated hydraulic press. Pressure was applied until water began to be squeezed out of the sample. Pressures were typically in the 10 MPa range. The cylinders were trimmed to 5.0 cm in length and then allowed to sit overnight at room temperature before being cured at 120 C. This so called “soaking” is

typically used to allow time for dissolution and for geopolymer precursors to form (Breek, 1974; Dyer, 1988). The 40°C samples were cured in a “walk in” chamber that was maintained at 60% relative humidity. The 120°C samples were cured in sealed Parr type vessels fitted with Teflon liners at 120 °C for varying periods of time.

Concentrations used for road construction (table 7) are lower.

Quantity of NaOH (g)	Water quantity (litre)	Concentration (g/l)	Molarity
100	5	20	0,5M
200	5	40	1M
400	5	80	2M
800	5	160	4M

Table 7. Composition of solutions used in alkali activation of Feral for road construction

3.4 Mechanical tests

The Californian Bearing Ratio (CBR) test done on Feral gives a value of 13%. This value is obtained after 3days conservation in air and 4days immersion in water of the compacted sample. Or the minimum requirements CBR for a material to be use in road construction is 80% for substructure and 30% for sub-base.

Then, we explore a treatment of Feral with cement. For soil treated with cement, the minimum requirements for CBR are 160% for substructure and 6-80% for sub-base.

3.4.1 Compressive strength

After different periods of curing, the mechanical behavior of the cylinders was tested. The compressive strength values were measured after 6, 12 and 24 h for the samples cured at 120°C.

3.5 Durability tests

In order to test durability, pieces of three samples cured at 120°C for 12 h (#s 2, 9, 16) were ground to sizes less than 150 µm and more than 75 µm and then dried at 105 °C. One gram of each of the powdered specimens was placed in 10 mL deionized water and held at 90°C for 1 and 7 days in a sealed Teflon container. This test is a modified product consistency test (PCT) designed to test glass leaching (ASTM C1285, 2008). These samples were chosen because it was assumed that reaction has reached the greatest degree at 120°C and leaching of these samples would better reflect what would happen to all bricks that had been cured for a longer time once it was used to build a house (some years).

4. Results

4.1 Physical and mechanical properties of Feral

The physical and mechanical properties of Feral are summarized on table 8 (Sy, 2000). Feral has an important fine content (24 % < 80µm). 13% of these fines are of clay size (≤ 2 µm). The CBR of Feral (13%) is low. According to table 4, the Feral must be treated for its use in the sub-base of road construction.

Grain size	
% > 2mm	10
% < 80µm	24 (26 after CBR)
% < 2µm	13
C _u	600
C _c	32
Sand equivalent (SE)	
piston	34
observed	30
Atterberg limit	
W _l (%)	32.6
W _p (%)	29.3
I _p (%)	3.3 (4.2 after CBR)
Activity (A)	0.25
W _{OPM} (%)	20.4
γ _{dmax} (kN/m ³)	18.3
CBR at 95% OPM	13
Swelling (%)	0
γ _s (kN/m ³)	27.6
γ _{app} (kN/m ³)	13

Table 8. Physical and mechanical properties of Feral.

4.2 Feral treated for road geotechnics

4.2.1 CBR of Feral treated with Portland cement

By adding cement in Feral (table 9), its bearing capacity is gradually improved enabling its use in sub-base.

CBR' (%)	94	-	110	164	257
CBR (%)	19	39	60	70	87
% of cement	1	1.5	2	2.5	3

CBR after 3days in air and 4days immersion in water - CBR' after 7days in air

Table 9. Evolution of Californian Bearing Ration with cement addition

We notice for CBR and CBR' an increase of bearing capacity with cement (Figure 3). But it shows also that the Feral is sensitive to water. This result can be explained:

- the material has been compacted at the modified optimum proctor and 4days of immersion will cause an excess of water,
- the infiltration of water after conservation at air (cause shrinkage) may provoke the weakness of the material due to cracks.

2 and 3% cement content give CBR conform to CEBTP standards for use of Feral in road substructure.

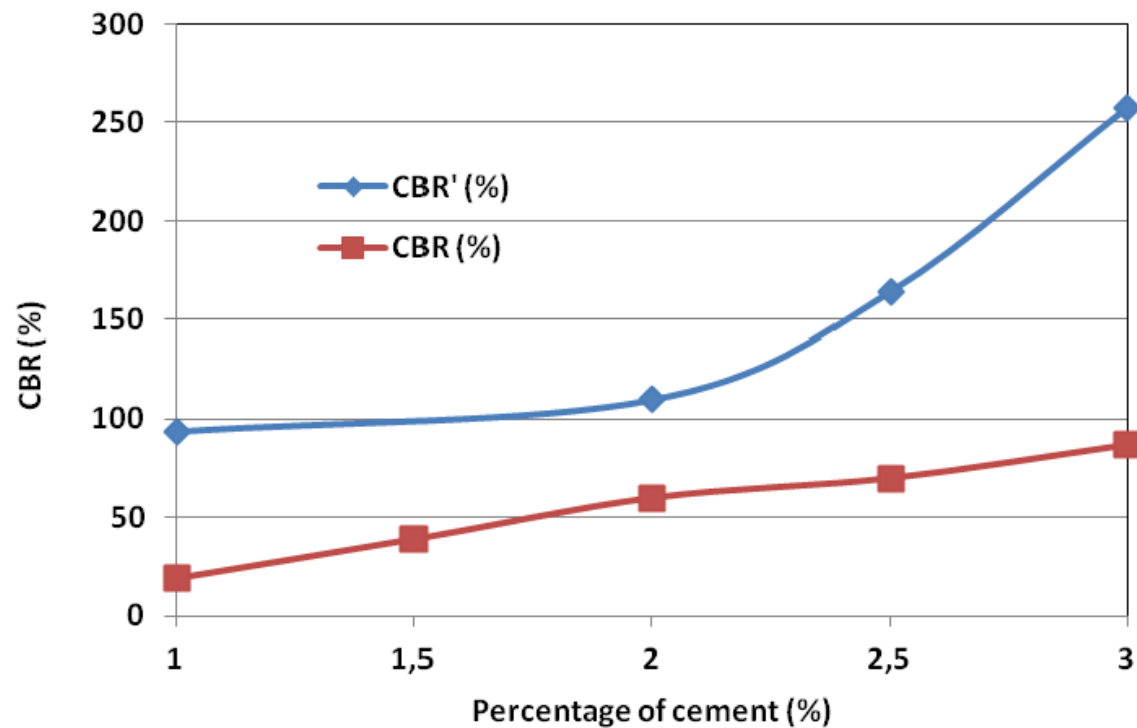


Fig. 3. Evolution of CBR with cement content

Figure 4 represent the evolution of strength with age for different cement content varying between 1 to 3%. No matter what the cement content, strength decrease with age.

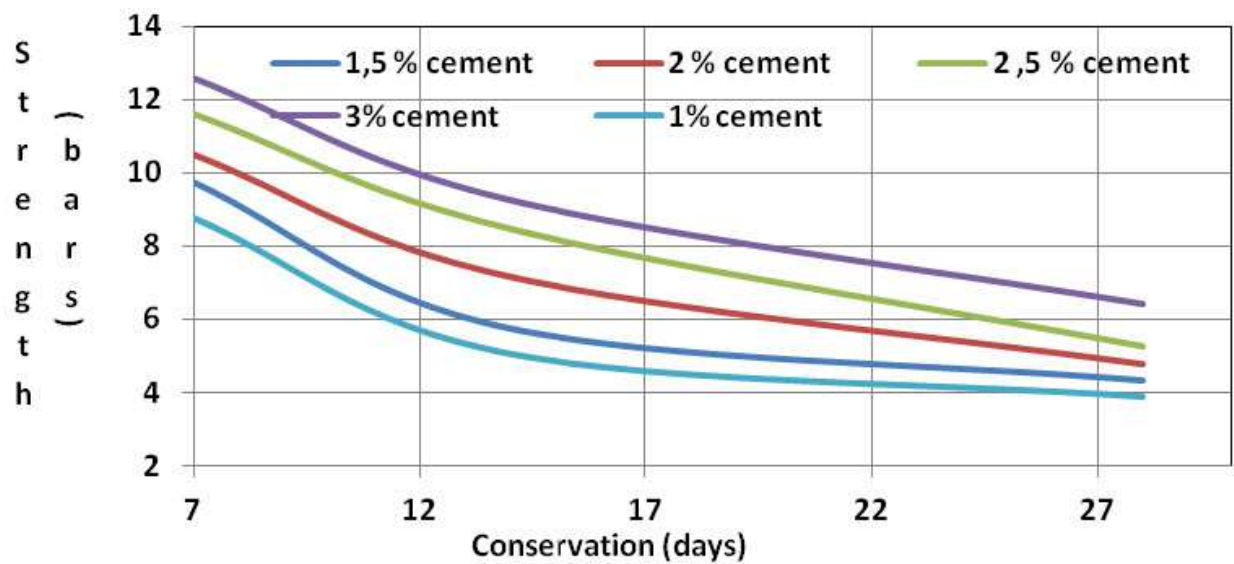


Fig. 4. Evolution of strength with age for different cement content

Figure 5 represents the evolution of CBR/CBR' with different cement content. The CBR/CBR' is an indication of the sensitivity of a material to water.

The values of cement between 2 to 3% give a soil-cement in conformity with CEBTP standard for a use in sub-base. However, compressive strength measurement is necessary to fully appreciate the aptitude of the material for road construction.

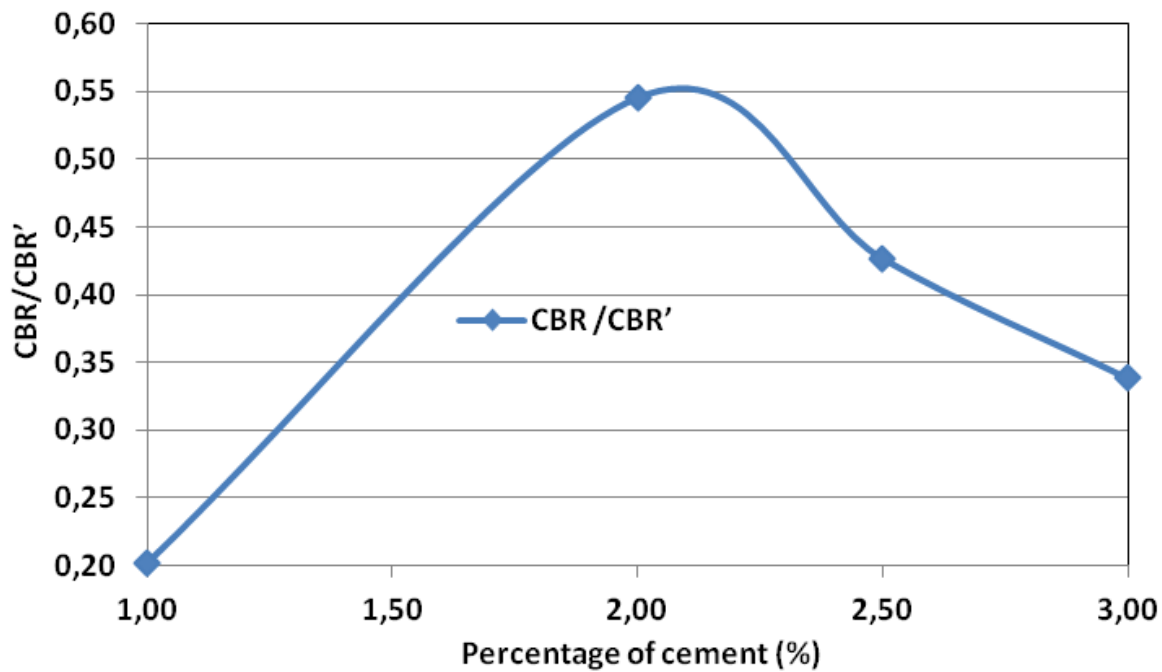


Fig. 5. Evolution of CBR/CCR' with different cement content

Improvement of Feral waste					
Compressive strength after 7days R_{c7} (bars)	8.76	9.74	10.51	11.59	12.58
Compressive strength after 14days R_{c14} (bars)	5.06	5.74	7.15	8.45	9.25
Compressive strength after 28days R_{c28} (bars)	3.89	4.32	4.75	5.24	6.41
R_{c7}/ R_{c28}	0.44	0.44	0.45	0.45	0.51
Percentage of cement (wt)	1	1.50	2.00	2.50	3.00

Table 12. Variation of Compressive strength functions of the age and cement content

Figure 6 represents the variation of compressive strength as a function of the age and cement content.

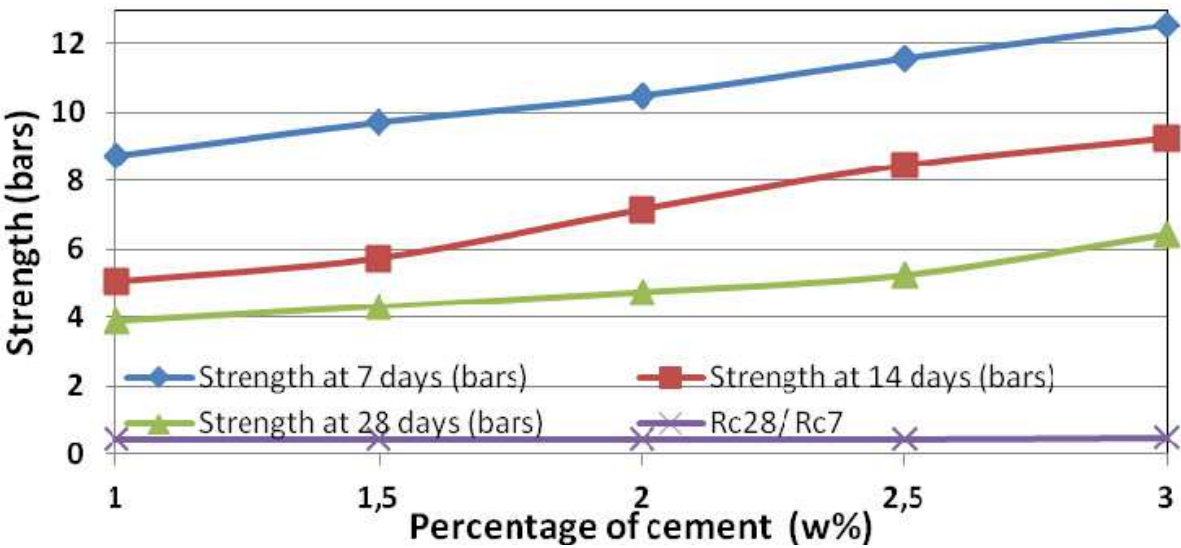


Fig. 6. Variation of Compressive strength function of the age and cement content

We notice for all cement content a decrease of compressive strength with age. The compressive strength after 28days is at least 45% less than the compressive strength after 7days. Hence, an alkali activation of Feral with concentrated caustic solution (NaOH and Na-Si) is tested.

4.2.2 CBR of alkali activated Feral

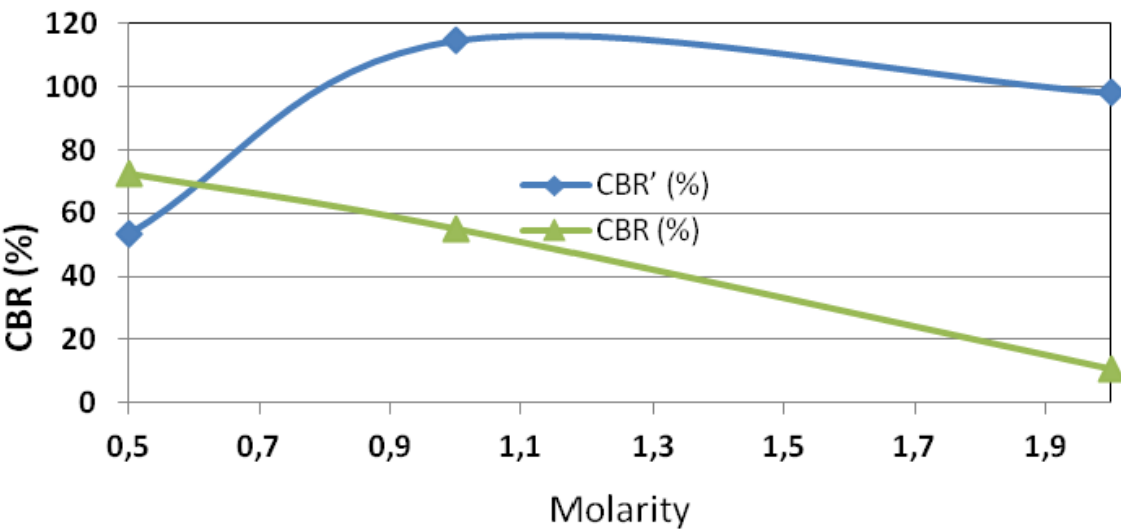
It was found that caustic addition caused zeolite minerals with aluminium-phosphorus-oxygen frameworks (AlPO_4) to form (Dyer, 1999). In the related aluminophosphates (AlPO_4), each negatively charged AlO_4 tetrahedron is balanced by a positively charged PO_4 tetrahedron, and non framework cations are not needed (Sherman, 1999). Still other variants include the silicoaluminophosphate (SAPO) structures in which Si substitutes some P in the AlPO_4 framework; each added Si needs a non framework cation to balance the charge on the framework. The results of alkali activation of Feral with concentrated caustic solution will be exposed in the paper.

Molarity	CBR' (%)	CBR (%)	Compressive strength after 3days in air and 4days immersion (bars)	Compressive strength after 7days in (bars)
0,5M	54,0	73	28	59
1M	115	55	31	65
2M	98	11	35	73

*CBR after 3days in air and 4days immersion in water - CBR' after 7days in air

Table 13. CBR* tests on alkali activated Feral

Either activated with 0.5M or 1M NaOH Feral can be used in road substructure. The same conclusion can be done for Feral Activated with 2M NaOH. Feral activated with these concentrations can't be used in road sub-base ($\text{CBR} \geq 160$).



CBR* after 3days in air and 4days immersion in water - CBR' after 7days in air

Fig. 7. CBR* tests on alkali activated Feral

4.3 Feral treated for the manufacture of bricks

4.3.1 Mechanical tests

Typical stress strain curves for Feral samples made with 4, 8 and 12 M NaOH solutions and cured at 6h, 12 h and 24h at 120 °C are given in figure 8. The deformation curve of the cylinders shows that the rupture is progressive. Breaking of the 2.5 by 5.0 mm cylinders during compression was good; all breaks exhibited a typical double pyramidal shape.

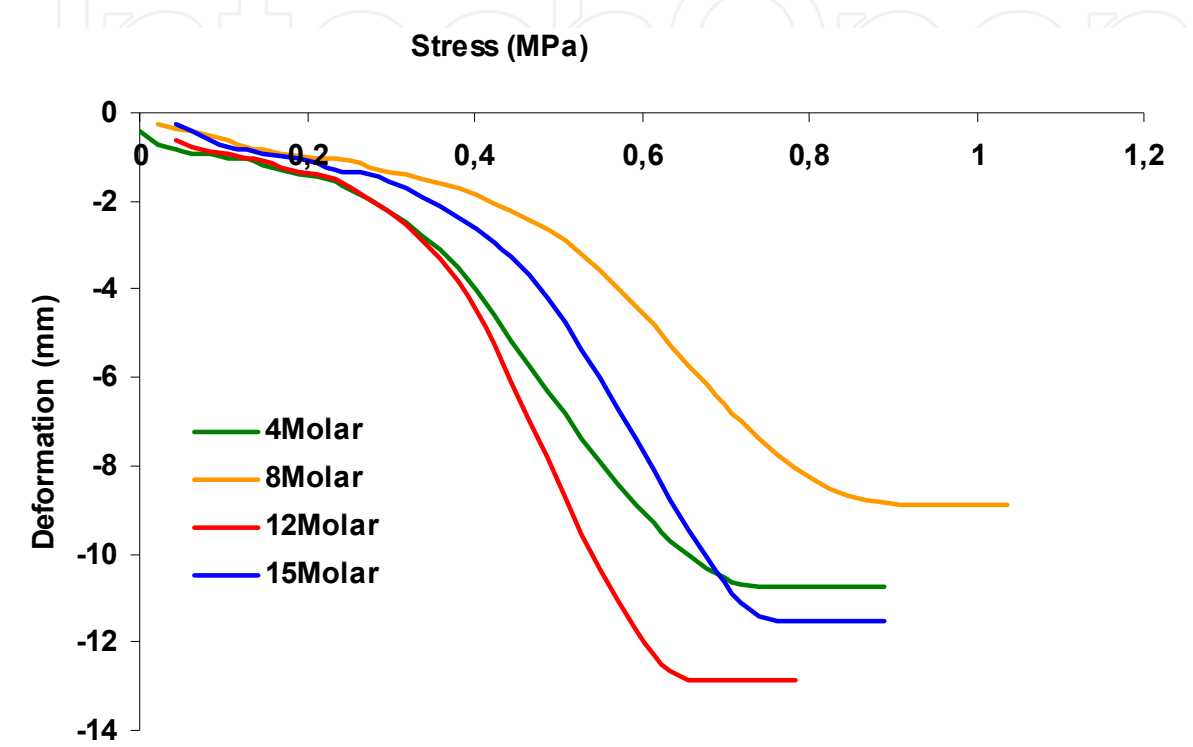


Fig. 8. Stress strain curves for samples made with 4, 8 and 12 M NaOH solutions as a thick paste and then cured at 120 °C.

A summary of the strength data is given in figure 8.

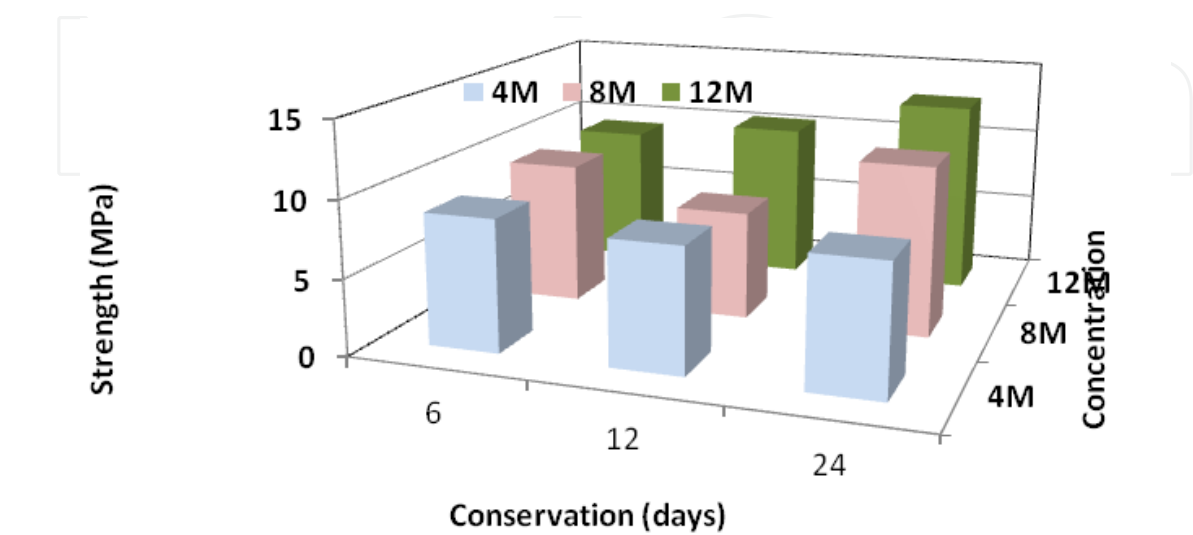


Fig. 9. Summary of compressive strengths of samples cured at 120 °C.

4.3.2 Physical and chemical analysis

Figure 10 represents a Micrograph microstructure of Feral treated with 12 M NaOH solution and cured at 120°C for 12 hours. The micro-structure is more columned-like texture. Based upon X-ray data in figure 11, it is proposed that these crystals are millisite.

Figure 11 represents the X-ray diffraction patterns for the 120 °C samples cured for 12 h made with different molar NaOH solution. The tabular crystals are the most common and based upon X-ray diffraction data presented are probably millisite. There is not very much difference between the patterns. There is a general broadening of peaks with increasing concentrations. Millisite $((\text{Na}, \text{K}) \text{CaAl}_6(\text{PO}_4)_4(\text{OH})_9 \cdot 3\text{H}_2\text{O})$ a zeolite phosphate is the most representative of forming minerals; then Huangite $(\text{Ca Al } 6(\text{SO})_4(\text{OH})_{12})$. Quartz (SiO_2) and Dickite $(\text{Al}_2\text{Si}_2\text{O}_5 (\text{OH})_4)$ are new silicate minerals. It is proposed that other zeolites are also present because of the reduction in the amount of starting materials, but that they are probably sub microscopic and thus not able to diffract X-rays in a coherent fashion.



Fig. 10. View represents the microstructure of the Feral treated with 12 M NaOH solutions and cured at 12 h.

Samples fabricated from Feral and NaOH solutions attain compressive strengths that range from 6 to more than 16 MPa (Fig. 9). These strengths are in the range of similar samples made with metakaolin. Strength development is dependent on temperature and length of curing, alkali concentration, fineness, and composition of the raw materials. The best mechanical performance of the samples depends of the concentration of NaOH solution used to make the sample. For 4 molar concentrations the greatest compressive strength is obtained after 12 hours curing. For 8 and 12 molar concentration the greatest compressive strength are obtained after one day curing. The strength given by the Feral treated with 15 Molar concentration and cured for 12 hours (8.35 MPa) is less than for the 12 Molar concentration and cured for the same duration (12.84 MPa). By using a mixture between "D" sodium silicate and 8 Molar NaOH solution (100g 8 Molar NaOH + 250g "D" sodium silicate), the compressive strength is neatly increased (16 MPa). This may be due to the fact that with "D" sodium silicate, we have both the formation of zeolite silicates and zeolite phosphates. The deformation curve of the cylinders shows that the rupture is progressive. Breaking of the 2.5 by 5.0 mm cylinders during compression was good; all breaks exhibited a typical double pyramidal shape.

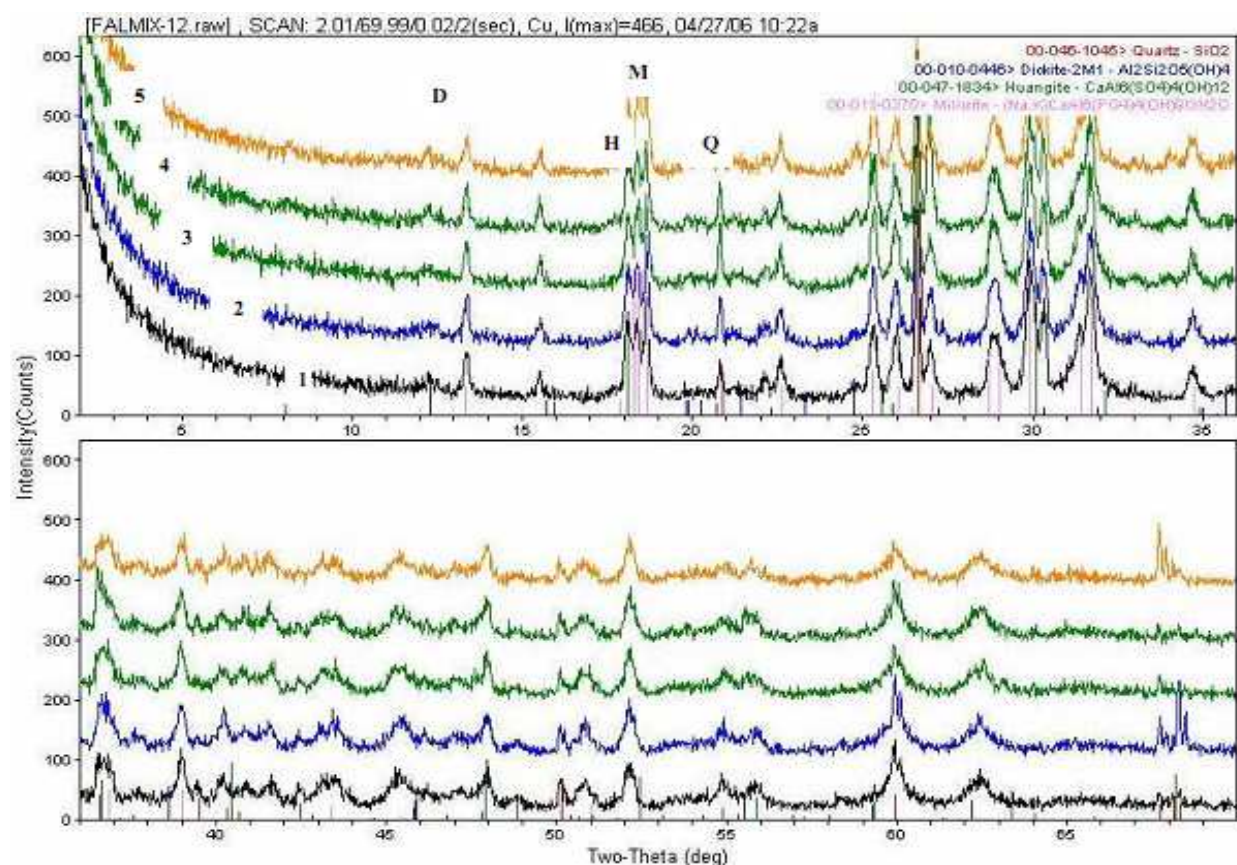


Fig. 11. Comparison of X ray diffractometer powder of Feral (curve n°1) and samples made with 4 (curve n°2), 8 (curve n°3), 12 (curve n°4) and 15Molar (curve n°5) NaOH concentration reacting with Feral after 12hours conservation. D = dickite, H = huangite, M = millisite, Q = quartz

Solubility tests were performed with Senegalese Feral reacting with caustic ASTM C1285 - 02(2008). Samples were ground to size less than 250 μm and 1 gram placed in 10 mL deionized water and held at 90 $^{\circ}\text{C}$ for 7 days. After 24 h, the leaching tests of the 120 $^{\circ}\text{C}$ samples showed very low conductivities no matter what concentration of alkali used to make the brick. The values of conductivities increased with time (Table 14), the one day conductivities for all three samples are lower than they are at 7 days. There is a kinetic process (possibly diffusion controlled) that limits the buildup of Na in solution. There is little Al or Si present in the solution, because these species are essentially insoluble; it is the sodium which accounts for the conductivity. For example a standard solution of NaOH in water with a conductivity of 1 mS/ cm contains 200 ppm NaOH (Bao and al 2005).

The 4 M and 8 M samples have the lowest overall conductivities, whereas the 12 M samples are almost twice as high. This suggests that the amount of Na in the 4 and 8 M brick reacts nearly completely, whereas the 12 M sample may contain excess NaOH or soluble sodium silicate which washes out giving it a higher conductivity and pH. The moderate pH confirms the formation of silicate minerals of some type. These values are in line with those one obtains when natural zeolites are put in water. Sodium does not leach from these minerals to any great extent. Nevertheless, all conductivity values are reasonably low, proving that reactions are occurring during curing and that zeolite-like mineral(s) are probably forming (Bao and al 2006). Solubility is low. Durability should be better.

Concentration (molar)	Measurement at 1 day		Measurement at 7 days	
	Conductivity (mS/cm)	pH	Conductivity (mS/cm)	pH
4	0.7	10	1.00	10
8	0.6	10	0.90	10
12	1.5	11	2.10	11

Table 14. Results of leaching test of bricks cured at 120 °C

5. Discussion

The treatment of Feral with cement using different percentage has permitted to appreciate the mechanical behavior of this material and its sensitivity to water.

The treatment of Feral with cement improves its bearing capacity but for the long term (7days, 14 days and 28days), strength decrease no matter what the cement content. This phenomenon may be caused by the high content in P₂O₅ (0.82) of the Portland cement used. The Feral itself coming from phosphate mineral treatment contain around 25wt% of P₂O₅. According to several studies, among them, those of Lafarge laboratories (Cochet, 1995) stating that P₂O₅ is a strong retarding agent for the setting and hardening of mortar. Percentage higher than 0.5 will causes a decrease of initial resistance and an increase of the setting time.

P ₂ O ₅ (%)	Resistance of mortar (French standards)		
	7days	14days	28days
0.05 - 0.55	*	*	c
0.05 - 1.10	**	*	■
0.05 - 1.55	***	*	■

* = decrease; ** = high decrease; *** = very high decrease; c = constant; ■ = increase; ; ■ = high increase

Table 15. Impact of P₂O₅ on the characteristics of cements

So other means of treatment should be explored.

Alkali activation of Feral present the main advantage in connection with its composition: SiO₂ (13wt %), Al₂O₃ (27wt %), P₂O₅ (25wt %), CaO (7wt %) and Na₂O (1.3wt %). The attack of Feral with caustic solution (sodium hydroxide and/or sodium silicate) will enable the formation of geopolymers and zeolite minerals with aluminium-phosphorus-oxygen frameworks (AlPO_{4s}). Forming mineral may include other variants like silicoaluminophosphate (SAPO).

The treatment of Feral with alkali makes it possible to use them in road substructure. However tests must be performed to determine the optimum concentration.

For bricks, Feral is treated with varying alkali concentration: between 4M, 8M and 12M.

For samples cured at 120 °C, regardless of the concentration of NaOH used, 12 h of curing gives the best compressive strength. This can be explained by the fact that with temperature, the reaction between the alkali solution and the Feral has taken place. After 12 h of curing,

the hydrated phase that forms are AlPO_4 type zeolitic, because the bulk composition of the starting material falls within a compositional range typical for zeolites. Although the zeolites minerals that form are not as “stable” as kaolinite, they are able to bond to each other and form a solid that is much more resistant to softening and deformation during annual wet/dry cycles. All zeolites are metastable to some degree (Sherman, 1999; Diop and Grutzeck, 2008). The ones that form first, in the presence of abundant water, will become less hydrated and undergo phase transitions as a result of diagenesis. If placed in an aggressive environment such as one with an acidic pH, they will also dissolve. In neutral and alkaline environments however they are very insoluble. Zeolites will change with geological time if buried, but if exposed to heat and humidity at the surface, this change is nearly imperceptible. The type of zeolite that forms during the manufacture of the aforementioned brick is somewhat temperature dependant. What will happen on occasion is that an initially formed zeolite will change into another one, one that is more stable. This is a problem associated with nucleation and growth from supersaturated solutions and is similar to what happens during diagenesis. Early formed zeolites are often the least stable converting to a more stable form after a few hours or days of curing. This makes it mandatory for the person making brick using this method (especially at 120 °C) to test strength versus time to see if a disruptive phase change occurs that could reduce performance by introducing shrinkage/expansion cracks. If these occur, samples should not be cured longer than necessary to achieve initial maximum strength.

For all the samples tested, those mixed with 12 molar NaOH had the highest strengths. This is what one might expect, because as one increases the concentration of the alkali solution more Feral will dissolve in the solution and more sodium aluminophosphate precursors will form that have the ideal ratio to form AlPO_4 , i.e. Na:Al:Si P = 1:1:1). However, increasing the concentration of NaOH indefinitely (e.g. 15 M) will not cause a continuous increase in the strength; rather it will cause more sodium rich phases to form that may not be as insoluble as zeolites. This will increase solubility and possibly have a negative effect on durability.

The strengths and leachabilities of the samples are similar to those for alkali activated metakaolinite samples which usually run about 3 MPa, have a pH of about 10 and a conductivity of 2-3 mS/cm (Breck, 1974) Bao et al, 2004; Bao and Gritzeck. The ability to make a brick with these characteristics is rather exciting because of its implications and potential impact on the nature of sun dried brick making in developing countries.

6. Conclusions

Zeolites are very insoluble. They are currently forming at the bottom of the World's oceans. However, the Na ions in a zeolite are mobile, which accounts for a zeolite's ability to exchange cations with other substances in solution. In this case the measurement of conductivity used here is actually measuring two things: the degree of reaction that the sample has undergone prior to being tested, and the mobility of the Na ion in the zeolitic-matrix as it exchanges with protons in the water (Bao et al, 2005). If the conductivity of the solution is low this suggests that the NaOH that was used to make the sample has reacted with the Feral and has been “tied up” in a tectosilicate matrix. Conductivity reflects the degree of fixation (effectiveness of the recipe to do what it is meant to do) and the magnitude of the cation exchange of Na^+ for H_3O^+ that takes place. It is safe to say that if no NaOH had reacted it would dissolve in the leaching solution and conductivity would be in

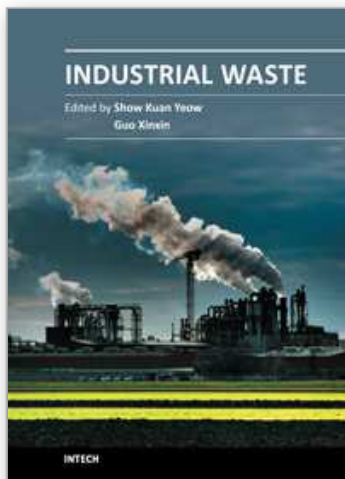
the 20-30 mS/cm range. Because we are in the 1-3 mS/cm range, this suggests that zeolites are forming and they are very much part of the structure even though their presence may not be evident in SEM or X-ray diffraction scans. Based on the low conductivity numbers of 120 °C samples, it is predicted that durability of the long term room temperature cured alkali activated Feral brick should be better than that of conventional sun dried clay brick.

The development of a quick temperature process to create durable bricks can be accomplished according to the needs of the community. The process does not generate chemical pollutants like fired clay bricks. It can use by-product materials like industrial waste enabling brick makers to solve environmental problems. A wooden mold and a mix of granular material and seawater (if commercially produced silicates are not available) are enough to fabricate good quality block with this technique. Locally available materials can be tested with different amounts of NaOH as mixing solution and cured as a function of temperature to determine the optimum concentrations of NaOH to use. At this time, we recommend 8 M NaOH because it seems to be a compromise between strength and cost. If a stronger brick is needed, one can use 12 M NaOH because strength was significantly higher in this case. This technology appears to be a solution for African developing countries like Senegal, but for the US too, if clean technology is desired. It seems possible that villagers could start their own businesses providing income and at the same time upgrading the brick used to build houses on a village to village basis. It is also proposed that a simple manual press might be used to make full sized bricks.

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This book is intended to fulfil the need for state-of-the-art development on the industrial wastes from different types of industries. Most of the chapters are based upon the ongoing research, how the different types of wastes are most efficiently treated and minimized, technologies of wastes control and abatement, and how they are released to the environment and their associated impact. A few chapters provide updated review summarizing the status and prospects of industrial waste problems from different perspectives. The book is comprehensive and not limited to a partial discussion of industrial waste, so the readers are acquainted with the latest information and development in the area, where different aspects are considered. The user can find both introductory material and more specific material based on interests and problems. For additional questions or comments, the users are encouraged to contact the authors.

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