+

PHOSPHOGYPSUM BASED CEMENT FORMULATION IN AGREEMENT WITH STANDARD PORTLAND CEMENT IN THE FRAMEWORK OF A CONCRETE CODE POLICY FOR THERMAL AND ENERGETIC EFFICIENCY OF THE BUILDING

Mouhamadou Bassir Diop [1,2], Awa Alioune Ndiaye,
Sosse Ndiaye, Bassirou Lo, Oumar[1,2] Sakho, Papa Douta Tall[1,2],
Aboubaker Chédikh Beye[1,2], and Wole Soboyejo[2]

1 Groupe de Physique des Solides et Science des Matériaux, Faculté des Sciences et Techniques, Université Cheikh Anta Diop de Dakar, Dakar-Fann Sénégal.
2 International Material Institute, Princeton Material Institute, Princeton university, NJ / USA

Abstract: Substitution of imported gypsum by phosphogypsum, a co-product of Senegalese production of phosphoric acid from phosphates has been achieved for the fabrication of the so-called Portland cement CEM II/A-M 32 R (European standards) containing up to 5% of gypsum.

The physical and the chemical aspects of the cement with phosphogypsum as sulfatating agent (high content of SO_3) respect Senegalese and European standards. However, the setting time of this phosphogypsum-based cement is found higher than that of the gypsum-based CEM II/A-M 32 R cement. Previous study shows that this increase is linked with soluble P_2O_5 present in phosphogypsum. A complete substitution of gypsum by phosphogypsum is possible in so far as all the standards have been fulfilled.

However, a substitution of 50% of gypsum by phosphogypsum still cost-effective, has been found more appropriate with respect to the setting time remaining inside an interval conform to the habit practitioners. The use of composite materials in general and phosphogypsum-based cement in particular is discussed the framework of a Comprehensive Concrete Code Policy for Thermal and Energetic Efficiency of the Buildings

KEYWORDS: cement, gypsum, phosphogypsum, sulfatating, resistance, setting time, Concrete Code, Thermal and Energetic Efficiency of the Buildings.

INTRODUCTION

The phosphate fertilizer industry produces 1.6 tons of phosphogypsum per ton of phosphoric acid as a by-product of such acid manufacture from phosphate ore. Phosphogypsum production (about 60 millions tons / year) is more than half of that of natural gypsum. Cement CEM II A-M 32.5 R, produced by the SOCOCIM – Industries is composed according to NS 02-006 and NF EN 197-1 of 80 -94 % of clinker, 6 – 20 % of addition except gypsum percentage which varies between 0 and 5% [1-6]. For a given clinker, the level of resistance of the cement is widely influenced by the total quantity of SO_3. It indeed exist for a given term, a rate of sulphate for which the resistance of the cement is maximal. Generally, and according to alkaline contained in the clinker, the optimal quantity of sulphate leading to the best resistance evolves according to the considered term (one day, 2 days, 7 days, 28 days). This sulphate results from the constituent gypsum of the cement, which is a regulator of hardening. In replacement of imported gypsum in Senegal, the glances are turned towards another product called phosphogypsum [7], available in large quantity in Senegal. It is therefore necessary to compare the gypsum with phosphogypsum in cement, and to determine the optimal SO_3 rate for powerful cement [8].

CHARACTERISTICS OF GYPSUM PHOSPHOGYPSUM AND GYPSUM BZSED POTLAND CEMENT

The chemical analysis of cement CEM II AM 32.5 R gives the chemical composition according to the major elements. The contents of the principal elements of cement and the mineralogical composition are summarized in table 1:

Other elements such as: chlorinate, Zinc, Phosphor etc can be present, but in general with very small percentages. These contents are distributed in various chemical phases generated starting from basic materials constitutive of cements [9].

Table 1: Chemical and mineralogical composition of cement II/ A-M 32.5R

Constituents	%	Symbol	Mineralogical elements	%
SiO_2	20 to 25	C_3S	Alite	55 –70
$Al_2 O_3$	2.0 to 7.5	C_2S	Belite	10 – 25
Fe_2O_3	1.0 to 4.5	C_3A	Aluminate tricalcic	0.5 – 13.0
CaO	64 – 70	C_4AF	Alumino-ferrite-tetracalcic	1 – 15
MgO	0.5 – 4.5	Free CaO	Free lime	0.5 – 3.0
SO_3	0.0 – 1.5	SK + SN	Alkaline Sulphates	0.2 – 2.2
TiO_2	0.1 – 0.6			
K_2O-Na_2O	0.3 – 1.5			
Free CaO	0.5 – 3.0			

Table 2: Mechanical and chemical exigencies of cement CEM II/ A-M 32.5R

Classes	**Compressive résistance (N/mm^2)**			
	Resistance at young age		Normal resistance	
	2 days	7 days	28 days	
	Inferior limit	Inferior limit	Inferior limit	Superior limit
32.5 R	10		32.5	52.5
Chemical specifications			***Exigencies (%)***	
Loss on Ignition			≤ 5.0	
Insoluble residue			≤ 5.0	
Sulphate (SO_3)			≤ 3.5	
Chlorine			≤ 0.1	

The characteristics of cement depend on the quality of the clinker stemming from the cru notably of its grindability and the percentage of used gypsum [10]. The grindability is the aptitude of a product for being powder. It can be quantified by the energy needed to reach a given fineness. The factors influencing the grindability of the clinker are mainly:

- ✓ the percentage of belite (the clinker constituent the most difficult to crush) or the relationship between belite and alite. Any action aiming at limiting the content of belite results in a less power consumption.
- ✓ an improved clinker grindability with finer granulometry, when the SO_3 level of the clinker rises.
- ✓ The level of cooking taking into account that the temperature of cooking has a strong influence on the grindability. The triple effect of overcooking are mainly a decrease of grindability, a deterioration of the resistance and the time of hardening, a degradation of the production equipment. For a good grindability of the clinker, it is necessary to have a regular alimentation, a good aptitude for the combination (to have a good proportioning of the cru and a SO_3 level not too high), and a good flame.

At the natural state, the calcium sulphate is presented in the form of gypsum $CaSO_4$, $2H_2O$ or anhydrite $CaSO_4$. In fact, the gypsum layers are mainly exploited. The gypsum which appears generally in the form of rocks can also be met in the nature in the form of gypsum flowers. The average chemical formula of the gypsum is displayed in the table 3 as follow:

Table 3: Chemical analysis of gypsum

Chemical elements	SO_3	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	PF
Percentage	45.56	2.02	0.32	0	30.01	0.06	21.11

Grinding Tests

All the tests have been based on finding the specific energy necessary to obtain a given fine granulometry. This specific energy depends especially of the crystallography of the clinker and on the chemical composition [11].

The grindability or crushing is determined by comparing the increase in fineness in material fineness and the energy spent for such increase. In addition to the above mentionned parameters such as the SO_3 percentage, the level of clincker firing, the free lime rate is also an important factor governing the cement grindability.
Cement CEM II A-M 32.5 R consists of clinker, gypsum and calcareous addition [12]. Good quality cement is obtained for adequate fineness corresponding to a specific surface ranging from 3000 and 5000 Blaine (cm^2/g). The monitoring of quality control of cement is pre-requisite to start the study of the phosphogypsum-based cement.

Phosphogypsum, a by-product of phosphoric acid production:

The manufacturing process of the phosphoric acid at the I.C.S as depicted in figure 1, involves the formation of gypsum-rich residue.

$$\mathbf{Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \longrightarrow 10Ca\,SO_4,\ 2H_2O + 6H_3PO_4 + 2HF}$$

The daily production of gypseous residue is approximately 10,000 tonnes. The evaluation of the phophopgypsum stock shows an available quantity estimated to 167 millions m^3. It has a granulometry ranging from 0 to 100 µm, with 30 % of the grain size lower than 40 µm. Samples were taken on the phophopgypsum site and for chemical analysis.

The main impurities present in our phosphogypsum samples are phosphoric acid, sulphuric acid, and their related compounds. Moreover, one can note the presence of insoluble impurities such as silica and alumina, which are constituents without detrimental influence on the sulphating of the cement. The phosphorus compound varies from 0.3% to 3,5%. The quantity of soluble phosphate although small, remains sufficiently high to have an action on the hardening. The chemical analysis of phosphogypsum coming from the I.C.S. Darou exhibits an average composition as described on table 4.

Table 4 : Average chemical composition of phosphogypsum

Major constituents	SO_3	CaO	SiO_2	P_2O_5	PF
Percentage	42.26	30.33	4.23	0.52	21.14

The decomposition of gypsum, containing 46.5% of SO_3 is as follow:

$$CaSO_4 , 2H_2O \longrightarrow CaO + SO_3 + 2H_2O$$

According to table 4, the average composition of SO_3 is equal to 42.26% in the phosphogypsum. The relative sulfating characteristic of the phosphogypsum is equal to the ratio 42.26 / 46.5 = 91% comparable to that of gypsum.

Influence of the presence of phosphogypsum in cement:

Ten formulations have been made with phosphogypsum (from 1% to 10%) replacing gypsum in the CEM II/A-M 32.5 R. After having ensured a possibility of substitution of the gypsum by phosphogypsum according to their similar sulphating characteristics, it proves to be necessary to seek with which percentage this substitution is possible. A series of crushing was then carried out, to give a fixed percentage of addition (20%), the total content of phosphogypsum and clinker being 80%.
The mixture is crushed during 12 minutes in a ball mill. The duration of crushing has been selected according to the desired fineness (3000 m^2/g corresponding to the so-called surface specific Blaine or SSB).

Laboratory and industrial tests have been achieved. The laboratory tests include three parts: the research of adequate phosphogypsum percentage, the investigation on the cement grindability and the study of the influence of the phosphogypsum on the cement properties.

The SO_3 rate increases with that of phosphogypsum. The percentage of phosphogypsum brought into play lies between 1% and 7%, le&ading to a cement with a SO_3 content lower than 3.5 as specified in the standard. We note that the ignition loss is lower or equal to 6.5%. The free lime is on average equal 1%. The greatest value of MgO is 2.36%. The percentage of phosphogypsum must be lower than 8%, to give cement whose P_2O_5 content is lower than 0.5 (standard value).

Figure 4 shows that Blaine specific surfaces are higher than 3500 m^2/g; thus the grinding is fine to very fine (3504<SSB>6045). Time of the beginning of the hardening are very high compared to the time of normal beginning of hardening, which is 60 mn as figure 15 indicates it. The weight with the liter is lower or equal to 980 g.

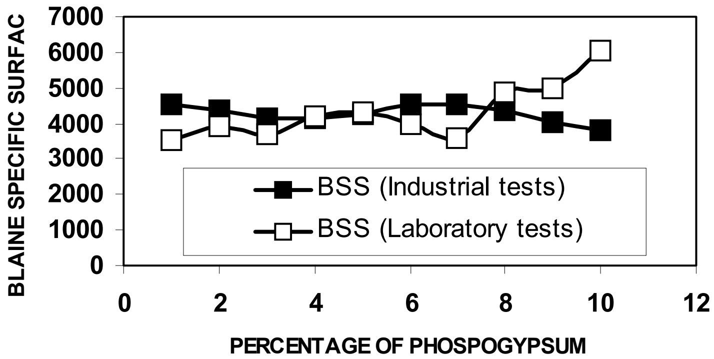

Figure 4 : Blaine specific surface and beginning of time of hardening for laboratory

The analysis of the curves of figure 5 shows two zones of fall corresponding to atypical values of Blaine specific surface and of beginning of hardening raises a problem of homogeneity. This one can be related to a phenomenon of filling of the balls or draining.

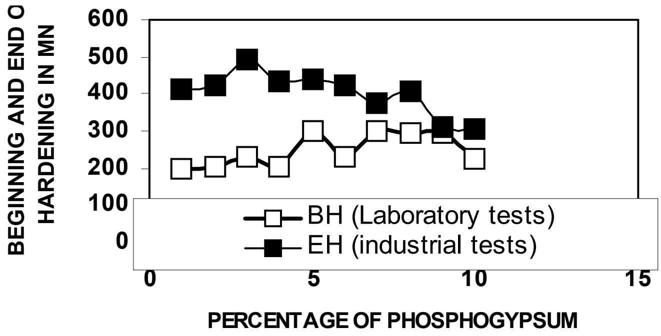

Figure 5 : Begining and end of hardening time as a function of phosphogypsum content

The compressive mechanical resistance measured after 2, 7 and 28 days are displayed in figure 6 as a function of phosphogypsum content. After 2 days, the compressive resistances (superior or equal to 10 Mpa) of all the phosphogypsum-cement samples are in accordance with the Senegalese standards (NS 02-006). At 7 days of maturation, all the samples with phophogypsum are in conformity with the values obtained usually, because their resistance are higher or equal to 22 Mpa. On the other hand, after 28 days of conservation, only the samples with 3% to 10% of phosphogypsum are in conformity with the Senegalese standards, their resistances ranging from 32.5 MPa to 52.5 MPa.

These results show that the percentages of phosphogypsum in conformity with the standard range between 3% and 10%. The optimum value is found for a phosphogypsuym content of about 4%. It is necessary to study the cement grindability according to the phosphogypsum content, because it influences the energy consumption.

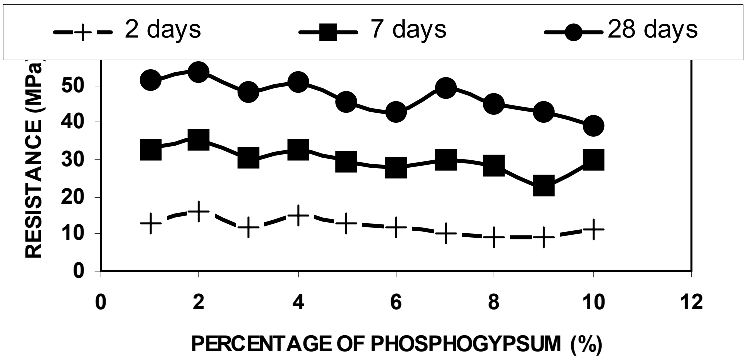

Figure 6: Resistance as a function of phosphogypsum percentage (laboratory tests)

Taking into account this optimum value (fineness corresponding to 3,500 BSS) of the phosphogypsuym content, the grindability-related specific energy has been measured for phosphogypsum percentage from 0 to 3%. Moreover, a decrease of the specific energy decrease with the incresase of phosphogypsum content has been observed.

Coming to the phosphate compounds, if the action of phosphorus and phosphates are rather well known when they are present in the cru as minor elements of the clinker, their action as an addition in cement is not well studied.

The P_2O_5 content in the starting mixture has been evaluated and compared with the P_2O_5 content in the crushed cement. It has been found that the variation of the P_2O_5 in the samples lies between 0.73 to 0.40. This variation is weak compared with that of the phosphogypsum ranging between 3.5 and 0.3. Even at small content, the presence of the P_2O_5 has a noticeable influence on the physical and chemical properties of cement. As all soluble phosphates, P_2O_5 has a powerful hardening-retardation capacity. In fact, the action of the P_2O_5 depends on the cation with which it is associated and the solubility of the salt thus obtained.

To study the influence of the P_2O_5 on the physical behaviour of cement, we undertook two experiments. The first one consists of adding variable percentage of sodium phosphate (Na_3PO_4), a phosphoric acid salt; the second experiment consists in adding a percentage of phosphoric acid, an acid of third degree, in the CEM II A-M, 32.5 R cement.

Each of them reacts with water to form phosphate ion $(PO_4)^{3-}$ that are soluble in the medium.

$$Na_3PO_4 + 3H_2O \rightleftharpoons 3Na^+ + (PO_4)^{3-} + 3H^+ + 3OH^-$$

$$H_3PO_4 + H_2O \longleftrightarrow PO_4)^{3-} + 4H^+ + OH^-$$

The soluble $(PO_4)^{3-}$ reacts with cement influencing the hardening time as seen in figure 7.

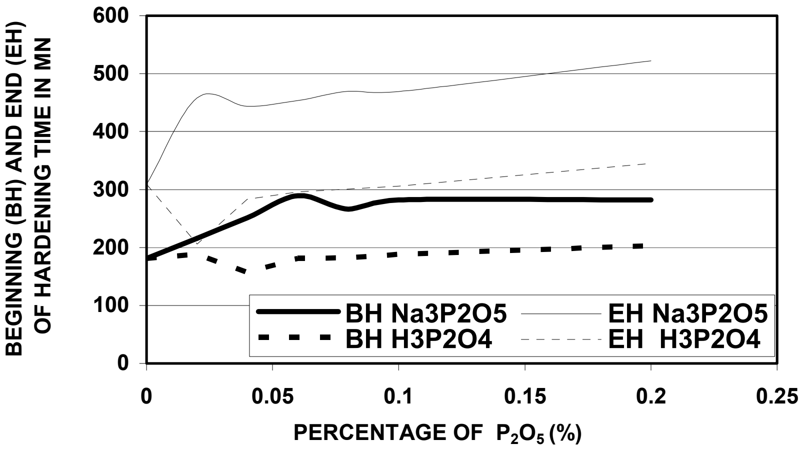

Figure 7: Variation of time of hardening in function of % P_2O_5
(BH and EH stand for begining and end of hardening respectively)

With weak P_2O_5 content (< 0.04%), the **hardening-beginning time** increases from 182 mn to 200 mn for the cement with phosphoric acid (bold dashed curve) and from 181 to 296 mn for the cement with sodium phosphate (bold continuous curve). For P_2O_5 content above 0.04%, the beginning time of hardening stabilizes slightly below 300mn and 200 mn respectively.

For the cement with phosphoric acid (fine dashed curve), between 0 and 0.06% of P_2O_5 content, the **end of hardening** decreases from 300 mn, undergoes a minimum slightly above 200mn, and increases again up to 350 mn from 0.06% to 0.2% of P_2O_5. With sodium phosphate (fine continuous curve), the time of hardening shows a strong increase from 300mn up to 470mn for P_2O_5 content varying between 0 and 0,2%; the **end of hardening** then decreases after this value, undergoes a minimum, and then rises to end at 520 mn for 0.2%. of P_2O_5.

Generally, according to the Senegalese standard (NS 02-020), the time of beginning of hardening for cements of class 32.5, 32.5 R, 42.5, 42.5 R, must be equal at 20°C to 60 minutes at least [15]. The increase of the time of hardening between 0 and 0.02% is explained by the influence of soluble phosphate.

Large scale tests (industrial tests) were led in the crusher. The study consists in the total replacement of gypsum by phosphogypsum, searching for the optimum percentage of phosphogypsum for a good quality cement. For that purpose, a variable percentage of phosphogypsum (0 to 10%) was used. The main impact of the phosphogypsum addition in cement is the increase of SO_3. According to the Senegalese standards NS 02-006 and NS 02-020, the cement CEM II/ A-M 32.5 R must have a sulphate rate lower than 3.5% [1,12]. Thus for the respect of this standard, the phosphogypsum percentage must be lower or equal to 5%.

The presence of other compounds which may affect the cement quality has also been investigated. The highest value found for MgO is equal to 0.78%, lower to 5% (max value in the senegalese standard). As for chlorine Cl, a percentage of 0.027%, has been fond below the standard maximum of 0.1%. This enables to testify that the standards are fulfilled by the cement formulations.
The granulometry control shows a refusal on the 40 µm sieve between 16.2% and 19.1%. The measured Blaine specific surface

has been found superior to 3200 m^2/g, falling in the average fine to medium grinding.

The compressive mechanical properties has been investigated and the result of the industrial tests as a function of phosphogypsum content are displayed in figure 8.
For the resistance at 2 days, only the samples with phophogypsum percentage lower than 4.5% are conform to Senegalese standards NS 02-006 [1]. Their resistance are superior or equal to 10 MPa. After 7 days of maturation of tests bars, only samples with phosphogypsum percentage between 0 and 10% are conform to standards with the values obtained in laboratory, their resistance being superior or equal to 22 MPa.

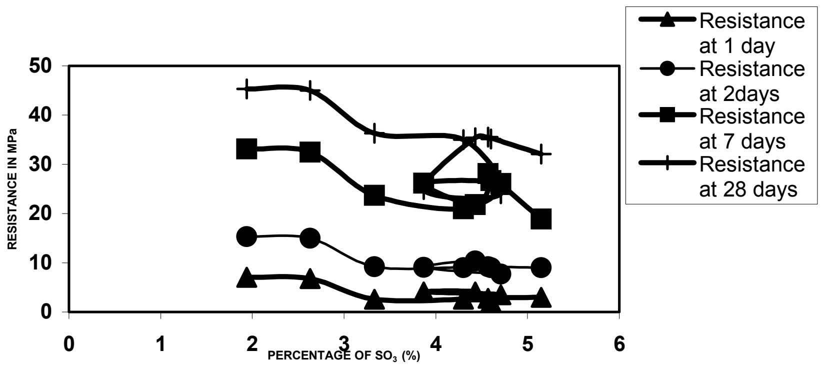

Figure 8: Compressive resistance in function of % of phosphogypsum of industrial tests

At the age of 28 days, only the samples with phosphogypsum percentage between 0 and 9.5% are in accordance with the standards, their resistance being superior to 32.5 Mpa [1]. Furthermore, the optimum phosphogypsum percentage range (2.85% to 4.5%) for a 2 days resistance is similar to that of 28 days. Thus the sulphating optimum is limited to this interval. The values of SO_3 corresponding to this interval are lower than 3.5%, as indicated in the Senegalese standards NS 02-006 and NS 02-020 [1,15].

SOME CONCLUDING REMARKS ON CONCRETE CODE POLICY FOR ENERGETIC AND THERMAL EFFICIENCY OF BUILDINGS

An analysis of meteorological data and climatic zone partition has been achieved for hygroscopic and thermal comfort in Sénégal in the framework of a west-africa regional project supported by the United Nation Development Program (UNDP) and the World Environment Funds (WEF). This project dealt with the reduction of greenhouse gas emissions by improvement of energetic efficiency of buildings in West-Africa

An approach based on Thermal Balance Analysis and determination of transmission coefficients of the wall building as a function of material properties, building orientation with respect to the sun exposure, wind permeability, thermal inerty, etc. has been taken succesfully. It has been found after an energetic auditing of existing building that 20% of the electricity consumption is due to bad insulation, exposure, location of windows and doors, lack of appropriate shadow masks, etc.. A concrete code policy including these above mentioned aspects is on the way of implementation.

CONCLUSION

The performance appraisal of the industrial and laboratory tests allow to appreciate the capacity of the phosphogypsum to replace the gypsum, as a regulator of hardening. With the report that the standards were respected for the resistance and for the sulphating. The addition of the phosphogypsum in variable percentages in the laboratory and industrial tests allowed seeing the influence of the product, on the parameters illustrating the quality of the cements. All the parameters are in accordance with the standards, the phosphogypsum appears as a substitute of the gypsum at level of 3 to 4.5% of constituents. Nevertheless, times of hardening are high comparatively to those whom we usually obtain with the gypsum; but corresponding to the Senegalese standards. This rise is due to the presence phosphate. Les us remind that the phosphate as such does not influence the hardening of cement, but it's it soluble part which acts on the hardening time. The more the soluble par, the more the acidity the more the hardening time In order to not perturbate the habit of use, an equal proportion of phosphogypsum and gypsum is recommended.

Our study shows the importance of taking into account the global and comprehensive environmental aspects when laying out concrete code policy for building construction [17-19].

REFERENCES

1. Norme sénégalaise : NS 02 –006, Liants hydrauliques : Définitions, classification et spécification des ciments.
2. Norme EN 196 – 2, Méthode d'essai des ciments –partie 2 : Analyse chimique des ciments, (1995).
3. Norme EN 196 –4, Méthode d'essai des ciments –partie 4 : Détermination quantitative des constituants, (1994).
4. Norme ENV 197 –1, Ciment, Composition, Spécification et critères de conformité – Partie 1 : Ciments courants, (1992).
5. Norme NF P 15-487, Liants Hydrauliques : Méthode pratique instrumentale d'analyse des ciments par spectrométrie de fluorescence de rayon x, (1985).
6. LAFARGE, Formation – Action / Produit - *Centre Technique Inter- unités Procédés,* (1996).
7. PRAYON Rupel Technologies, Section conversion et qualité des sous-produits de Sulfate de Calcium ex-Phosphate de Taïba - *Test CPP, Central Prayon Proces,* (1996).
8. MASO J. C, La liaison entre les granulats et la pâte de ciment hydraté – *Rapport principal thème 7éme congrès International de la chimie des ciments à Paris* (1980).

9. FARRAN J, JAVELAS R., MASO J. C., PERRIN B. « Étude de l'auréole de transition existant entre les granulats d'un mortier et la masse de ciment hydraté» *Colloque RILEM Toulouse* (1971).

10. LAFARGE, Composition cru / Clinker - *Centre Technique Inter- unités Procédés,* (1999).

11. PECH M., BOURGEOIS M., L'Optimisation du broyage –vol 1 –Broyabilité, finesse et séparateurs (Nov 2001).

12. ESCADEILLAS G., Les ciments aux fillers Calcaires, contribution à leur optimisation par l'étude des propriétés mécaniques et physiques des Bétons fillérisés – *Thèse de Doctorat , université Paul SABATIER – Spécialité Génie Civil ,143 pages* (1988).

13. Norme EN 196 –1, Méthode d'essai des ciments – partie 1 : Détermination des résistances mécaniques, (1987).

14. Norme EN 196 – 3 – Méthode d'essai des ciments – partie 3 : Détermination du temps de prise et de la stabilité

15. Norme sénégalaise : NS 02 –020, Liants hydrauliques : Technique des essais – Essai de prise

16. PECH M.– Le broyage –VICAT : Ecole du ciment : Comprendre la production (Fev 2002).

17. Mouhamadou Bassir Diop, Awa Alioune Ndiaye, Sosse Ndiaye, Bassirou Lo, Oumar Sakho, Papa Douta Tall, Aboubaker Chédikh Beye, and Wole Soboyejo Evaluation of phosphogypsum as an alternative of gypsum in the fabrication of CEM II/A-M 32.5 R Portland Cement in Proceedings of the 6th International Congress on Global Construction: Ultimate Concrete Opportunities 5-7 July 2005 Dundee, Scotland, UK. Progress report of the Project entitled '' Reduction of greenhouse gas emissions by improvement of energetic efficiency of buildings in West-Africa Pool of Consulting-Expert to the United Nation Development Program (UNDP) :

Aboubaker Chédikh BEYE, Sossé NDIAYE, Bassirou LO, Physicists and Material Scientists Mbacké NIANG, architect and Cheikh KANE, Engineer (1999-2001).

18. Final report of the Project entitled ‘’ Reduction of greenhouse gas emissions by improvement of energetic efficiency of buildings in West-Africa Pool of Consulting-Expert to the United Nation Development Program (UNDP) : Aboubaker Chédikh BEYE, Sossé NDIAYE, Bassirou LO, Physicists and Material Scientists Mbacké NIANG, architect and Cheikh KANE, Engineer (2000-2002).