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Treatment of Phosphate and Phosphogypsum Samples and Prospectives for Phosphogypsum Valorization Stored in Senegalese Chemical Industries

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ABSTRACT

In this study, the aim is the treatment of phosphogypsum and phosphate sample collected in the senegalese chemical industries and actions of management for the valorization of the phosphogypsum. The treatment of phosphogypsum and phosphate show that naturally impurities are present in the samples and this chemical analysis of the treated of the phosphogypsum established improvement of the quality of it. The values observed of MgO, SO_3, P_2O_5, in the phosphogypsum were 24.811%, 57.054% and 1.763% respectively and 35.166%, 0.741%, 53.225% in the sample phosphate if the device is calibrated with standards type mining. The toxic elements found in our study were Mercury, Lead, Cadmium, and Arsenic if we calibrated by standards of mining type, thier activity is low than limit detection of the device for the gypsum, while in sample phosphate, we find a very low quantity of Arsenic and Cadmium equal to 08,860 ppm and 48,380 ppm respectively, when we calibrated with soil type standards, the concentrations of Mercury, Lead and Cadmium are not detectable, while for Arsenic the value was 09,550 ppm for Phosphogypsum and 03,040 ppm for Phosphate. The major phases Alite (C_3S), Belite (C_2S), Aluminatetricalcic (C_3A), and Tetra-calcium aluminoferrite (C_4AF), and control ratios Lime Saturation Factor (LSF), Aluminium/Iron ratio (AR), and Silica ratio (SR) were measured. These experimental results shown that the C_3S, C_2S, C_3A, C_4AF, LSF, AR and SR contents fulfilled the requirement of the Jordan Standards and European Standards. The acidity of samples, was an unfavourable parameter for geotechnical and mechanical properties due to the impurities, The data show that the evolution of densities as a function of compaction energies was not analogous to that of sand, mainly because of the fragility of phosphogypsum crystals as the compaction energy increases, the crystals break and the fragments fill the inter-granular voids.

Introduction

The production of phosphoric acid used mainly in the phosphate fertilizer industries induces a sub-product called phosphogysm. It is well known that natural phosphates contain various stable and radioactive elements that could be of environmental concern to the public (Chang et al., 2008). Phosphogypsum is a calcium sulphate containing some impurities coming essentially from the ore. Five tons of phosphogysm are produced for every ton of phosphoric acid manufactured (Al-Hwaiti et al. 2010). Approximately 58% of the worldwide phosphogysm is stockpiled, 14 % is reprocessed and 28% is dumped into water bodies (FIPR, 1998). The problems of pollution generated by this product were discussed by many authors in the world (H. sfar Falfoul, et al. 2002). (Phosphogypsum) which also may be used as agricultural gypsum to deal with salinity, because the high radioactive contents may lead to a significant exposure of manufacturers and end users (Saueia and Mazzilli, 2006). Especially in the chemical industries of Senegal (ICS), we note huge quantities of phosphogypsum stored, therefore actions of management and valorization are necessary. That's why after presented the gypsum and phosphate sample and thier treatment, we quote the various fields of valorization on the use in some particular fields such as the construction field. For the wet process, naturally impurities are present in the phosphate rock focused in phosphogypsum, including fluoride, sulfate, phosphates, organic matter, heavy metals, radionuclides, and residual acidity (Neville, 1996). In this study we made a treatment of phosphate and phosphogypsum samples take from in the Senegalese Chemicals Industries (SCI) using a portable X-ray fluorescence which is in the Instituve Technologies of Nuclear Applied (ITNA) in order to valorize the gypsum deposited for various purposes in the field of Senegalese construction.

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Materials and Methods

Humidity calculation

Moisture is the presence of water or water vapor in the air or in a substance (linen, bread, chemicals, wood humidity, etc.). The percent humidity for the phosphate and phosphogypsum samples was calculated using the following formula.

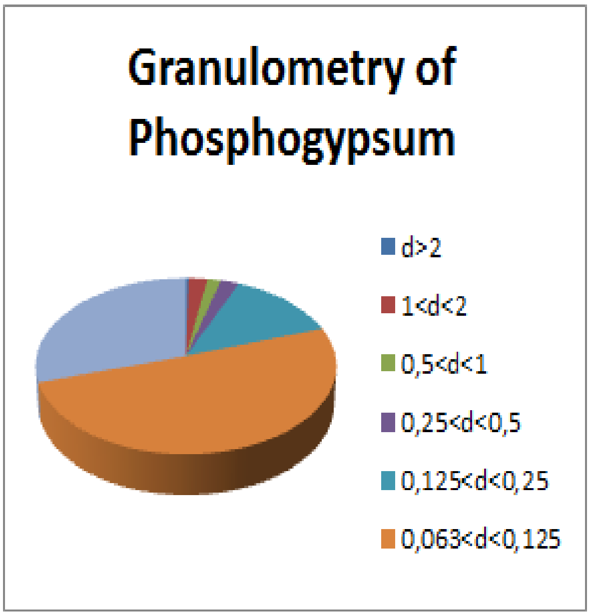
$$H(\%) = \frac{M_{before} - M_{after}}{M_{before}} \times 100 \qquad \text{Equ.1}$$

M_{before} and M_{after} are respectively the mass before drying and after drying. Weighing 50g of phosphogypsum and 50g of phosphate after drying we obtain 43.77g and 42.44g respectively, which representing a moisture of 15.12% for the phosphate and 12.48% for the phosphogypsum sample. These results show that the phosphate samples are wetter than the phosphogypsum samples, this may be due to the difference in sample sizes.

Granulometry

For study the granulometry, 200g of phosphate and 200g of phosphogypsum were weighed. With the help of the sieves and their different sizes, the results of the remaining masses and their percent are shown in the following table.

The results show the phosphogypsum has a granulometry of 49.960% equivalent to the sieve sizes between 0.063 to 0.125 mm and the phosphate sample the granulometry is equal to 30.322% with the sieve sizes of 0.125mm to 0.25mm. These results can be illustrated on the following figure.



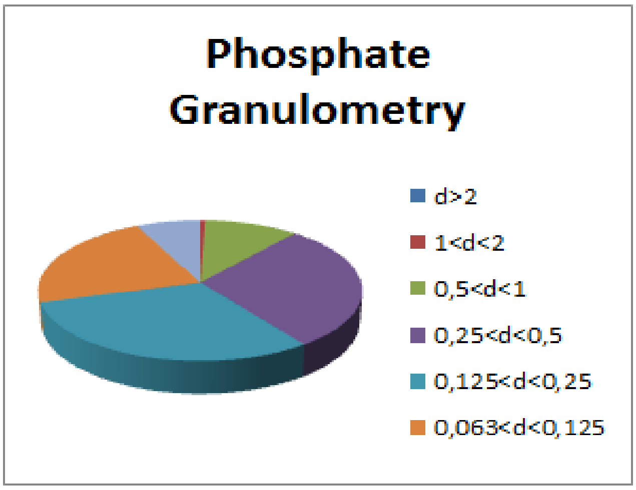


Figure1 . Granulometry of phosphogypsum and phosphate samples.

Study of hydraulic conductivity

The Mini Disk infiltrometer allows the measurement of the hydraulic conductivity of phosphogypsum and phosphate samples. The infiltrometer has been used by demonstrating the basic concepts of unsaturated samples. The upper chamber (or bubble chamber) controls the aspiration, the lower chamber is labelled as a graduated cylinder with the volume indicated in mL. The bottom of the Infiltrometer has a porous sintered stainless steel disc that does not allow water to leak into the air. The small disc allows measurements to be made without disturbance on relatively flat floor surfaces. Once you place the Infiltrometer on the sample the water starts to leave the lower chamber and seeps into the matrix at a rate determined by the hydraulic properties of the soil (Dohnal et al. 2010). As the water level drops, the volume is recorded at 30-second intervals. In the laboratory X-fluorescence, a test was done for phosphogypsum and phosphate sample, the results are given in table 2.

Table 2 . Infiltrometer data for phosphogypsum and phosphate.

Time(s)	sqrt of (s)	Volume (mL)	Infilt (cm)
0	0,00	80	0,00
30	5,48	68	0,75
60	7,75	59	1,32
90	9,49	50	1,89
120	10,95	43	2,33
150	12,25	35	2,83
180	13,42	28	3,27
210	14,49	22	3,65
240	15,49	16	4,02
270	16,43	10	4,40
300	17,32	05	4,72
330	18,17	01	4,97

Table 1 . Study of the granulometry by sieving of phosphogypsum and phosphate.

Sieves sizes (mm)	Remaining Mass of Phosphate (g)	Mass of phosphate (%)	Remaining Mass of Phosphogypsum (g)	Mass of phosphogypsum (%)
$d > 2$	0	0	0,659	0,329
$1 < d < 2$	1,050	0,525	4,425	2,212
$0{,}5 < d < 1$	20,887	10,440	3,185	1,592
$0{,}25 < d < 0{,}5$	57,778	28,881	4,350	2,175
$0{,}125 < d < 0{,}25$	60,660	30,322	26,250	13,124
$0{,}063 < d < 0{,}125$	44,414	22,201	99,930	49,960
$d < 0{,}063$	14,338	7,167	58,765	29,380

Time(s)	Sqrt of time (s)	Volume (mL)	Infilt (cm)
0	0,00	80	0,00
30	5,48	75	0,31
60	7,75	71	0,57
90	9,49	67	0,82
120	10,95	64	1,01
150	12,25	61	1,19
180	13,42	58	1,38
210	14,49	56	1,51
240	15,49	53	1,70
270	16,43	50	1,89
300	17,32	47	2,07
330	18,17	44	2,26

According to these results, phosphogypsum absorbs faster than phosphate because at 330 seconds the volume of water in the infiltrate remains 44 ml, while that of phosphogypsum remains 0.1 ml, this can be explained by the difference in particle size of the two types of samples.

We have drawn the correlation curves of the cumulative infiltration as a function of the square root of time. The following Figure 1 and Figure 2 summarize the infiltration tests for the phosphogypsum and phosphate samples with thier correlation coefficients of 0.9987 and 0.9984 respectively.

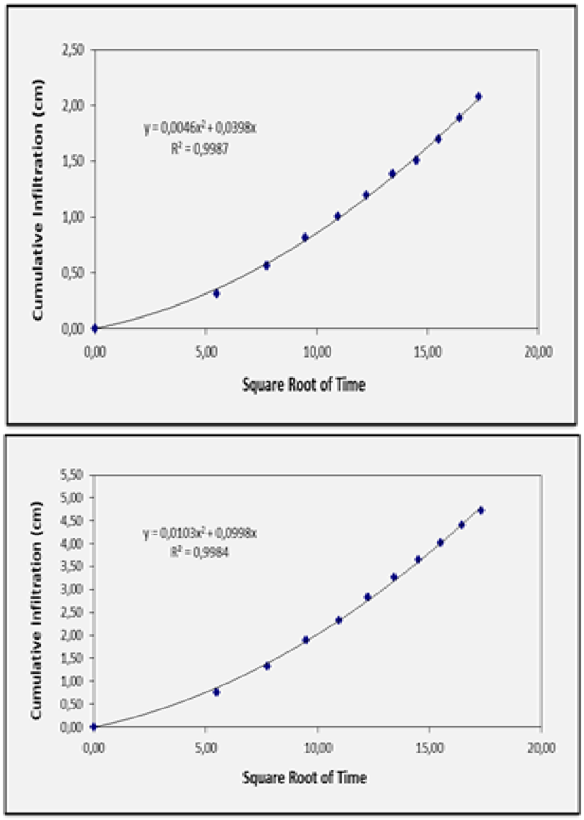


Figure 2. Cumulative Infiltration Curve for phosphogypsum and phosphate sample

Calculation of the porosity

A number of methods are available to determine the hydraulic conductivity of the soil from these data. The method proposed by Zhang (1997) is quite simple, and give good measurements of infiltration in samples. The method requires the measurement of cumulative infiltration as a function of time. The porosity K is calculated by the following formula:

$$K = \frac{C_1}{A} \qquad \text{Equ.2}$$

With

C_1: the slope of the cumulative infiltration curve as a function of the square root of time.

A: is a value linking the Van Genuchten parameters for a sample type

Where n and alpha are the Van Genuchten parameters, r_0 is the disk radius and h_0 is the suction of the disk surface. Van de Genuchten parameters for 12 soil texture classes and A values for a radius of 2.25 cm with suction values that vary from 0.5 to 7 cm. These values are summarized in the Table 3 with a variation of alpha for the different types.

In our study we have choosed a clay soil texture, after the calculations, the results show a porosity of 0.00220369 cm/s and 0.00108801 cm/s for phosphogypsum and phosphate respectively with the values of slopes C_1 equal to 0.009476746 for phosphogypsum and 0.004678871 for phosphate. These results show that phosphogypsum conducts water faster than phosphate, this can be caused by the fine particle size of the phosphogypsum.

X-ray fluorescence analysis of phosphogypsum and phosphate samples

Collection of samples

The samples were collected from the chemical industries of Senegal (ICS), with a quantity of 1000g of phosphate and phosphogypsum put in closed plastic bags and transported to the laboratory.

Samples Preparation

Once in the laboratory, samples are drying in the oven at 80°C, during 24 h.

Table 3 . Parameters Van Genuchten.

	radius	2,25	A							
	alpha	n / ho	-0,5	-1	-2	-3	-4	-5	-6	-7
sand	0,145	2,68	2,835701	2,40407	1,727908	1,241921	0,892621	0,641565	0,46112	0,331427
loamy sand	0,124	2,28	2,9853	2,786831	2,4286	2,116417	1,844363	1,60728	1,400674	1,220625
sandy loam	0,075	1,89	3,877062	3,887982	3,909913	3,931969	3,954148	3,976453	3,998884	4,021441
loam	0,036	1,56	5,461148	5,717657	6,267384	6,869965	7,530482	8,254505	9,048139	9,918077
silt	0,016	1,37	7,921451	8,177401	8,714378	9,286617	9,896433	10,54629	11,23883	11,97683
silt loam	0,02	1,41	7,102076	7,367933	7,929874	8,534674	9,185601	9,886173	10,64018	11,45169
sandy clay loam	0,059	1,48	3,210664	3,523317	4,242925	5,109507	6,153081	7,409796	8,923184	10,74567
clay loam	0,019	1,31	5,857535	6,10902	6,644845	7,227667	7,861609	8,551155	9,301181	10,11699
silty clay loam	0,01	1,23	7,893227	8,094056	8,511175	8,949789	9,411007	9,895994	10,40597	10,94223
sandy clay	0,027	1,23	3,336287	3,570465	4,089288	4,683501	5,364059	6,143508	7,036218	8,058649
silty clay	0,005	1,09	6,076318	6,169307	6,359575	6,55571	6,757895	6,966316	7,181164	7,402639
clay	0,008	1,09	3,998056	4,096399	4,300401	4,514562	4,739389	4,975412	5,223189	5,483306

Figure 4 . Sample preparation in the laboratory.

The samples are analyzed by a portable X-ray fluorescence device with a resolution of 178 eV@MnKα. The device is composed of an excitation tube of 50Kv, 40µA with a maximum power of 2W, the diameter of the beam of the apparatus is 7mm and a filter with a list of targeted elements as Ag source (Sb, Sn, Cd, Pd, Ag, Mo, Nb, Zr, Sr, Rh, Bi, As, Se, Au, Pb, W, Zn, Cu, Re, Ta, Hf, Ni, Co, Fe, Mn, Cr, V, Ti, Th, U) and an Al, Ti, and Mo sandwich for the elements Ba, Sb, Sn, Cd, Pd, Ag. A Cu filter for the elements Cr, V, T, Ca, K and finally for the elements Al, P, Si, Cl, S and Mg no filter.

Results and Discussions

Validation of the XRF method

After obtaining the results by measuring in ppm, the elements were converted to % by dividing by 10000. A comparison between phosphate and phosphogypsum measurements was made using a calibration that was performed with standards of mining origin. The following Table shows the concentration of the major elements (%).

A similar protocol was used for the phosphogypsum and phosphate samples and using soil standards for calibration. The following table shows the major elements for the soil type calibration

X-ray fluorescence analysis of phosphate and phosphogypsum shown that Calcium, Magnesium, Sulphur, Silicon, Aluminium, Phosphorus and Iron are in the majority, with minority elements such as Molybdenum, Uranium, Thorium and Potassium. Here phosphate and phosphogypsum are analyzed with a calibration performed with mining-type standards. However, if calibrated with soil-type standards, the major elements are Iron, Calcium, Sulphur, Titanium and Strontium for both types of samples. The major elements are summarized in the following table

After the major elements in the phosphate and phosphogypsum samples, we are also interested in the toxic elements and finally to evaluate the dangers or advantages that result from them.

Chemical substances are part of our daily life. All living or inanimate matter is composed of chemical substances and

Table 4 . Validation of the XRF method for the determination of elements Majors in phosphogypsum and phosphate.

NIST1646		Phosphogypsum(Mining Type)	Phosphate (Mining Type)
Al	2,297 ± 0,018 %	2,874 ± 0,420 %	6,469 ± 0,466 %
Ca	0,519 ± 0,020 %	26,263 ± 0,097 %	33,500 ± 0,120 %
Mg	0,388 ± 0,009 %	14,962 ± 2,334 %	21,206 ± 2,016 %
P	0,864 ± 0,016 %	0,270 ± 0,023 %	11,615 ± 0,055 %
Si	40,000 ± 0,016 %	7,564 ± 0,057 %	09,801 ± 0,066 %
S	0,352 ± 0.004 %	22,850 ± 0,057 %	0,297 ± 0,008 %
Ti	0,456± 0,021 %	0,0289 ± 0,014 %	0,029 ± 0,001%
Fe	-	0,058 ± 0,003 %	1,409 ± 0,014 %
Mn	-	0,032 ± 0,002 %	0,057 ± 0,003 %

Table 5. Validation of the XRF method for the determination of major elements with NIST1646.

NIST1646		Phosphogypsum (Soil Type)	Phosphate (Soil Type)
Ca	0,519 ± 0,020 %	25,330 ± 0,056 %	36,197 %
S	0,352 ± 0,004 %	15,605 ± 0,122 %	0,130 ± 0,070 %
Sr	0,006 ± 0,000 %	0,071 ± 0,001 %	0,118 ± 0,030 %
Ti	0,456 ± 0,021 %	0004 ± 0,001 %	0,040 ± 0,001 %
Zr	-	0,006 ± 0,001 %	0,009 ± 0,001%
Fe	-	0,054 ± 0,002 %	1,502 ± 0, 012 %
Zn	0,004 ± 0,001 %	0,001 ± 0,000 %	0,041 ± 0,001 %

Table 6. Average concentration of major elements in phosphogypsum and phosphate calibrated with mining standards.

Type Mining	Ca	Si	Mg	S	Al	P	Fe
Phosphogypsum	26,263 %	07,564 %	14,962 %	22,850 %	02,874 %	0,270 %	0,058 %
Phosphate	33,500 %	09,801 %	21,206 %	0,297 %	06,469 %	11,615 %	1,409 %

Table 7 . Average concentration of major elements in phosphogypsum and phosphate calibrated with soil standards.

Type Soil	Ca	Si	S	Fe
Phosphogypsum	36,197 %	0,118 %	0,130 %	1,502 %
Phosphate	25,30 %	0,071 %	15,605 %	0,054 %

the manufacture of almost all products involves the use of chemical substances.

When used properly, many chemicals can make a significant contribution to improving our quality of life, health and well-being. But others are very dangerous and, if poorly managed, can have a harmful effect on health and the environment.

This is why in our study we took into account the concentration of these toxic chemical elements in our two types of samples calibrated with mining-type and soil-type standards. The toxic elements found are Mercury, Lead, Cadmium, and Arsenic. Calibrating with mining-type standards gives the results in ppm in the following table:

Table 8. Values in ppm of toxic elements in phosphogypsum and phosphate calibrated with mining standards

	Hg	Pb	As	Cd
Phosphogypsum	-	< LOD	< LOD	< LOD
Phosphate	-	< LOD	08,860	48,380

According to these results, the values of Lead, Arsenic and Cadmium in phosphogypsum are below the limit of detection of the device, while in phosphate, we find a very low quantity of Arsenic and Cadmium equal to 08,860 ppm and 48,380 ppm respectively, so we can say that these elements can not cause dangerous effects for health and environment as if calibrated with soil type standards. The following table shows the measurements of the toxic elements in both types of samples**.**

Table 9.Values in ppm of toxic elements in phosphogypsum and phosphate calibrated with soil standards

	Hg	Pb	As	Cd
Phosphogypsum	< LOD	< LOD	09,550	< LOD
Phosphate	< LOD	< LOD	03040	< LOD

The results show that when calibrated with soil type standards, the concentrations of Mercury, Lead and Cadmium are not detectable, while for Arsenic the value is 09,550 ppm for Phosphogypsum and 03,040 ppm for Phosphate. Therefore it can be concluded that the phosphate and phosphogypsum samples haven't negative effects on the environment and human health.

We also find in these samples of phosphogypsum and phosphates other elements such as : chromium, manganese, molybdenum, etc. The quantities of this elements are present in both types of samples in low quantities, hence their name trace elements: theoretically, these are elements in lower concentrations than the major elements.

The composition of major oxides in the phosphogypsum and phosphate samples using mining standards was determined using the formulas below :

$$\%C_aO = \frac{\%C_a(A_{ca} + A_O)}{A_{Ca}}$$

$$\%so_3 = \frac{\%S(A_s + 3A_O)}{A_S}$$

$$\%s_iO_2 = \frac{\%S_i(A_{si} + 2A_O)}{A_{si}}$$

$$\%Fe_2O_3 = \frac{\%Fe(2A_{Fe} + 3A_O)}{A_{Fe}}$$

$$\%\mathrm{Al_2O_3} = \%\mathrm{Al}(\frac{2\mathrm{Al} + 3\mathrm{A_O}}{\mathrm{A_{Al}}})$$

$$\%P_2O_5 = \frac{\%P(2A_p + 5A_O)}{A_p}$$

$$\%T_iO_2 = \frac{\%T_i(A_{Ti} + 2A_O)}{A_{Ti}}$$

$$\%M_nO = \frac{\%M_n(A_{Mn+}A_O)}{A_O}$$

The following table summarizes the chemical composition of the oxides in the Senegalese phosphate and phosphogypsum samples.

According to the studies already done in the laboratory on the variety of senegalese cement, we noted that the variation of oxides in chemical composition in different varieties of cement available in the Senegalese, the quantity of CaO if we refer to the European standard for cement is in the range 61-67% (Tamas K. S., 2010**).** Study Aid 1,2-construction/building material 1 for Bsc (Civil and Architect Engineering). Ybl Miklos College of Technology, Department of Building Materials and Quality Control, Hungary). The amount of CaO is equal to 36.768% and 49.900% for phosphogypsum and phosphate respectively if we calibrated with mining-type standards and 29.121% and 50.675% respectively if the device was calibrated with mining-type standards, none of the phosphate and phosphogypsum samples are in this range. The EU stipulates in its specification document that S_iO_2 is in the range 19-23%, It has been observed that all three varieties samples are in this range within the specified limit, in our study the values of S_iO_2 in phosphogypsum wasn't in this range but in the phosphate sample the value was 16.131 % if we calibrated with mining type standard. The same standard states said that the sum of CaO + SiO_2 in cement should not be less than 50% by mass in a similar way also the ratio between CaO and SiO_2 should not be less than 2.0. The cement results shown that the sum of CaO + SiO2 is greater than 50% and the ratio between CaO and SiO_2 is greater than 2.0. The values of CaO + SiO_2 is less than 50% in the phosphogypsum sample and the ration is not less than 2.0. The amount of Al_2O_3 in several varieties of cement is between 2-6%, and for cement's study, none of the cement varieties is in this range. In our measurements we noted that the quantity of phosphogypsum sample and phosphate sample is in this range. The quantity of Fe_2O_3 according to the European standard is between 0-6%. Only Cement C is within this range, Cement A and Cement B are slightly outside this range in Sambou results, in our study the phosphate and phosphogypsum values are in this intervalle.

Table 10 . Chemical composition in (%) of Phosphate and Phosphogypsum samples calibrated in mining and soil standards.

	Phosphogypsum Type Mining	Phosphate Type Mining	Phosphogypsum Type Soil	Phosphate Type Soil
CaO	36.747 %	46.874 %	29,121 %	50,675
SiO_2	16.131 %	20.967 %	-	-
Al_2O_3	10.857%	24,438 %	-	-
Fe_2O_3	0.165 %	4.029 %	0,144 %	4,005
MgO	24.811 %	35.166 %	-	-
MnO	0.074 %	0.041 %	-	-
TiO_2	0.152 %	0.048 %	0,004 %	0,046
SO_3	57.054 %	0.741 %	18,206 %	0,152
P_2O_5	1.763 %	53.229 %	-	-
ZrO_2	0.006 %	0.006 %	-	-

The figure below summarizes the values of the phosphate and phosphogypsum samples calibrated with mine-type standards in (%).

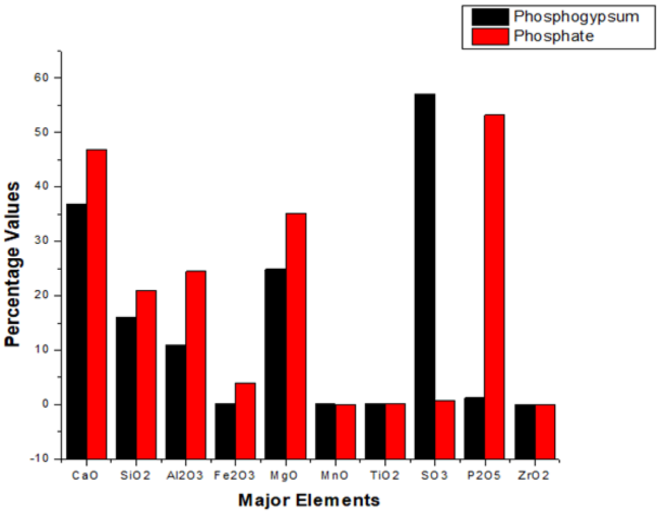


Figure 5. Percentage of major oxides in phosphogypsum and phosphate calibrated to mining.

The use of phosphogypsum in construction requires minimum mechanical resistance, especially in traction. We have verified the criteria required by the "Guide Technique des Traitements des Sols : (GTS" and the "Guide Pratique de Construction Routière) : Assises traitées [Charfi Fouratif F. et al 2000), for use in foundation courses.

Phosphogypsum is mainly composed of gypsum (75 to 78% for the dihydrate process) mixed with calcium phosphate in different forms, silica and other impurities such as iron, magnesium and aluminum oxides, sulfides, sulfides, calcium sulfate and other impurities organic matter and traces of metals (Charfi F. et al. 1999). The following table gives the chemical composition of the oxides in the Senegalese and Tunisian phosphogypsum samples.

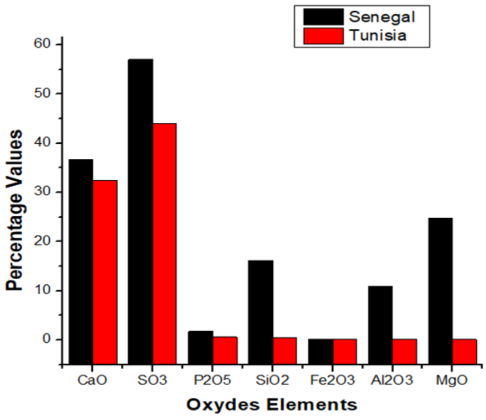


Figure 6. Variation for oxydes elements in senegalese and Tunisian phosphogypsum

Solubility of phosphogypsum

In our study we have not calculated the ph, but we know the solubility of phosphogypsum depends on the pH of the solution in which it is immersed. In demineralized water it is about 2.40 g/l (2.25 g/l for gypsum, according to Murat (CRCI 1977).

The results show that acidity, due of impurities, is an unfavourable parameter for geotechnical and mechanical properties (Mehta P. et al. 1977). The acidity of phosphogypsum should therefore be reduced, or even eliminated, in view of its sustainable use in pavement base courses. As it is necessary, for reasons of construction (Cescas Mp, 1999), to add aggregates larger than phosphogypsum, one can use a crushed limestone sand (Haerter M. 1968).

The mineralogical composition can be determined from the results in the table above. The BOGUE calculation is used to calculate the approximate proportions of the two types of samples. It is based on the amount of the dominant mineral available in phosphate or phosphogypsum. The following formulas refer to the composition in major elements subdivided into four groups which are C_3S, C_2S, C_3A, and C_4AF.

Bogue Calculation

$$C_3S = 4.071C_aO - 7.6S_iO_2 - 6.718A\ell_2O_3 - 1.43Fe_2O_3 - 2.852SO_3$$

$$C_2S = 2.867S_iO_2 - 0.7544C_3S$$

$$C_3A = 2.650A\ell_2O_3 - 1.692Fe_2O_3$$

$$C_4AF = 3.043Fe_2O_3$$

The Silicates C_3S and C_2S are the most important components; they are responsible for the strength of the hydrated cement paste. The presence of C_3A in cement is undesirable. C_4AF is also present in the cement in small quantities and compared with the other three components, it does not affect the behavior of the cement in a very significant (Ali, M., al. 2008). It is important to remember that these assumed compositions are only approximations of the actual compositions of the minerals.

The Silicn Tricalcium (3CaO SiO2), Silicon Dicalcium (2CaO SiO2), Aluminium Tricalcium (3CaO Al2 O3) and Iron Aluminium Tetracalcium (4CaO. Al_2O_3 Fe_2O_3) (Natalya G. Shanahan, 2003. Influence of C3S content of cement on concrete sulfate Durability. A Thesis submitted to college of engineering, University of south Florida). After BOGUE calculation and the major element composition contained in the following table, the proportions in % of C_3S, C_2S, C_3A and C_4AF calcium in phosphogypsum and phosphate are as follows:

Table 11. Chemical composition of oxides in Senegalese and Tunisian phosphogypsum.

Elément (%)	CaO	SO_3	P_2O_5	SiO_2	Fe_2O_3	Al_2O_3	MgO
Senegalese Phosphogypsum	36.747	57.054	1.763	16.131	0.165	10.850	24.936
Tunisian Phosphogypsum	32.500	44.000	0.650	0.500	0.100	0.100	0.100

Table 12. Variation in silicate and calcium concentrations of samples.

Type	**C_3S**	**C_2S**	**C_3A**	**C_4AF**
Phosphogypsum (Mining Type)	48,546 %	08,741 %	05,230 %	0,103 %
Phosphate (Mining Type)	61,467 %	10, 243 %	10, 538	02,550 %
Phosphogypsum (Soil Type)	50,988 %	38, 465 %	0,243 %	0,438 %
Phosphate (Soil Type)	200,130 %	150,978 %	06,776 %	12,187 %

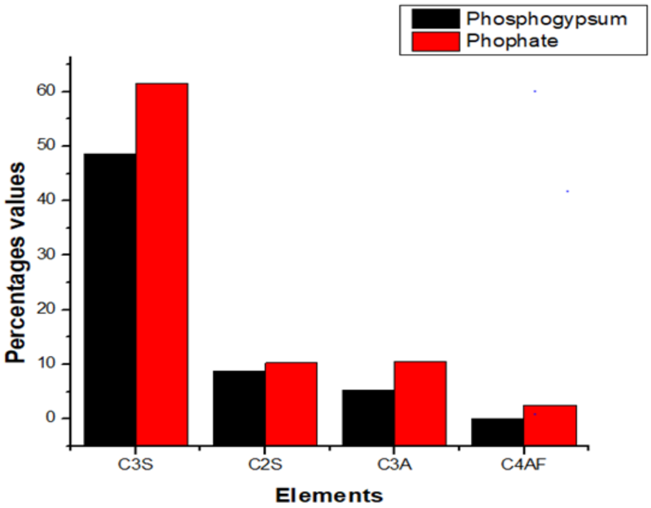


Figure 7.Major components in phosphate and phosphogypsum samples in mining calibration.

The percentage of C_3S in the phosphate and phosphogypsum samples is not in the range that has been admitted by the European Union standard (EN 197-1) for phosphate and phosphogypsum with their values 61, 67% and 50.988% respectively, this interval is 50-64%. The same European standard recommended a range of 14.2-18% for the proportion of C_2S, none of the samples of the different types are in this range, the values of phosphogypsum and phosphate calibrated with standard in mining type are respectively below this range and those of phosphate and phosphogypsum beyond for the proportions of C_2S. There is also the proportion of C_3A, which according to EN 197-1 is between 6-9%, an evaluation of the results showed that no sample is in this range of proportion of C_3A except the phosphate in soil mode with a percentage 06.776%. For C_4AF also, all the proportions found are outside the range recommended by the EU 8-12% except for the phosphate in soil type with a value approximately equal to 12.187%. The data show that the evolution of densities as a function of compaction energies is not analogous to that of sand, mainly because of the fragility of phosphogypsum crystals: as the compaction energy increases, the crystals break and the fragments fill the inter-granular voids. Phosphogypsum is a material with an evolutionary character during compaction. The variation of the chemical composition in constituting cements affects physical factors such as stiffness, hydration capacity, process time, corrosion resistance, color of the cement (Ali, M. et al. 2008); (Pandey G. et al.1980); (Vogel A. et al. 1989). A text book of quantitative Inorganic Analysis, the English language book Society and Longmans, green and Co. Ltd. 5th edition]. A construction based on a cement with a very high proportion of C_3S will gain in strength with a very fast hydration factor capacity, very often as early as the first week of construction. On the other hand, buildings designed with a high proportion of C_2S will see an additional gain in strength after a fairly long time; to be more precise four weeks after the building is installed.

Generally cement with a high C_3S proportion will have a low C_2S proportion. Thus, a building constructed with cement containing a fairly high proportion of C_3A will have a faster reaction leading to a hydration factor on heating a few hours after mixing. Both C_4AF and C_3A contribute both to the strength of the cement after mixing and in contact with air. However, the proportion of B cement is below the European recommendation. If C_2S gives negative values by this BOGUE calculation, the clinker contains C_3S instead of C_2S. In this case: $C_3S = 3.8S_iO_2$ (El Mrabet et al. 2015).

If we refer in the results in the three variety of Senegalese cement, we quoted that the Senegalese phosphogypsum can be used for construction like the cement.

Quality control

For the determination of the quality of the samples a control report (LSF, SR and AR) was carried out for each type of sample according to the above formulas.

Lime Saturation Factor :

$$LSF = \frac{CaO}{2.85S_iO_2 + 1.2A\ell_2O_3 + 0.65Fe_2O_3}$$

Aluminium/Iron Ratio : $AR = \dfrac{A\ell_2O_3}{Fe_2O_3}$

Silica ratio : $SR = \dfrac{S_iO_2}{A\ell_2O_3 + Fe_2O_3}$

According to Nasir and Eletr in 1996, the Saturation Factor (LSF), the ratio of Silicon to Aluminum (see formula below) are important factors for the chemical control of the sample Nasir S. and Eletr H. 1997. The mineralogy and chemistry of cement and raw material in the united Arab Emirates. Department of Geology, Ain Shams University, Cairo, Egypt).

Table 12.Variation in Quality Control Items for Samples.

	LSF	SR	AR
Mining Phosphogypsum (Type Mining)	1,219	4,771	58,941
Phosphate (Type Mining)	1,120	2,355	5,384

The quality control of the samples is recorded in the table below (Put the name of the table). The interval allowed by the EU for AR is between 1.3-2.5. If this ratio goes up to a value above 2.5, this would lead to a rigid leg with a very rapid attainment of the strength of the material and if this ratio is below 1.3, then a very fluid leg is obtained, with a slow ability to attain strength and a low hydration capacity. In the case of the phosphogypsum and phosphate mining samples analyzed in Senegal, this ratio is above 2.5 which mean that phosphogypsum and phosphate have a very fast capacity to reach strength. The usual frequency for the SR ratio is between 2-3. For an estimated SR ratio lower than 2, heating-up becomes very easy, however, an excessive liquid phase will form and a low resistance capacity of the phosphogypsum or phosphate is obtained as their values are well above.

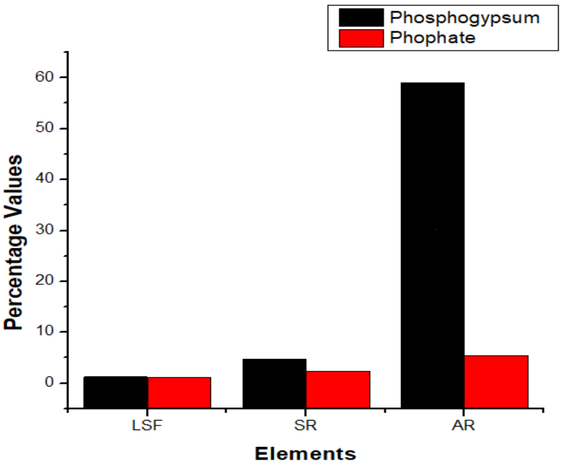


Figure 8. Diagram of Sample Quality Control Parameters.

Conclusion

The management of Senegalese phosphogypsum stored in chemical industries (ICS) is a difficult environmental problem to solve given the quantities produced and the chemical composition of the product. Taking into account the local context, it seems to us that a material recovery in road technology is possible for the realization of pavement or runway foundations in a region with little rainfall and relatively close to the production centers. Of course an economic analysis must refine this conclusion, and position this valorization in front of possible primary solutions such as the return to the mine or controlled storage. To increase the bearing capacity and mechanical resistance and to decrease acidity, we propose the addition of crushed limestone sand. To reach the mechanical resistances required by the regulations concerning pavement bases, it is necessary to further increase the mechanical tensile strength. We have only found that the addition of cement is necessary.

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