The effect of marl and clay compositions on the Portland cement quality

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Résumé: La qualité de clinker de ciment Portland dépend de la qualité des matières premières (calcaire, marne, argile ...) en particulier les marnes et les argiles. Ces matériaux sont les promoteurs de la qualité du ciment et les principaux contrôleurs du coût de production. L'usine des ciments de Bizerte a réalisé une étude complète des matières premières dans laquelle une variété d'argiles et de marnes ont été sélectionnés à partir de ses carrières et préparées pour différentes analyses (analyse chimique, absorption atomique, diffraction des rayons X, fluorescence X) afin d'élargir la gamme de matériaux existants et d'améliorer la gestion des carrières. Les résultats sont utilisées pour étalonner un spectromètre ARL 9900 installé dans le laboratoire.

Mots-clés: Clinker, Ciment Portland, matiéres premiéres, Argile, Marne, diffraction des rayons X, Fluorescence X, Etalonnage, ARL 9900.

Abstract: The quality of Portland cement clinker depends upon the quality of the raw materials (limestone, marl, clay…) especially marls and clays. These materials are the proponents of the cement quality and the main controllers of the production cost. Bizerte Cement factory has carried out a complete study of the raw materials in which a variety of clays and marls have been selected from its quarries and prepared for different analyses (chemical analysis, atomic absorption, diffraction X, fluorescence X) in order to expand the range of existing materials and improve the quarries management.The results are used to calibrate an ARL 9900 spectrometer installed in the laboratory.

Key words: Portland cement clinker, raw materials, Clay, Marls, calibration program, X-ray diffraction, X-ray fluorescence, calibrate, ARL 9900.

INTRODUCTION

Several researches have been made to improve the quality of the concrete, most of them are focused on the properties of the anhydrous phases present in the cement and their behavior during the hydration. It is known that the reactivity of the cement and clinker is mainly based on the reactivity of raw meal and therefore the reactivity of the raw materials [1]. Their use impacts the burnability of the raw meal, the chemistry of clinkering (additional minor elements), the burning profile and burner design, the refractory lining, the chemistry of emission, the properties of the doped clinker and its grindability, as well as the reactivity of the final product and its performances [2].

The aim of the present paper is to discuss the chemistry of the marls and clays and their influence on the properties of the raw powder. This subject was proposed by Bizerte cement factory, which seeks to extend its quarries. For this reason we have carried out a systematic study on the existing raw materials especially marls and clays.

In fact Portland cement is an equilibrium mixture of raw materials such as limestone, clay and other additives, according to their importance in the manufacture of cement, clays and marls come in second place after the limestone as raw materials. The prepared mixture or the raw meal is milled and calcined at 1450°C then the blend allows to obtain Clinker in which gypsum was

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added (a setting retarder) to get the Portland Cement [3]. The Portland cement clinker is mainly composed of calcium and aluminum silicate phases. Clays and Marls participate by the contribution of silica, aluminum and iron oxide necessary to perform the main mineralogical cement phases: **Alite (C3S), Belite(C2S), Aluminate (C3A) and Ferrite (C4AF)** [4]. These aluminum phyllosilicate materials contain also other elements such as Na_2O, K_2O, Cl and SO_3, as impurities which could affect the cement quality and even the process of its fabrication. Such elements can enter in the clinker composition and then condensate in the mineral phases and as a result affect the physico-chemical properties of the material [5]. At high concentrations these impurities could decrease the durability of concrete and even cause damage of the furnace [6].

In order to get a stable quality of the clinker, the quality of the raw material resources and the raw meal must be evaluated before undertaking a particular strategy for the burning and cooling processes. The chemical composition of these raw materials should be controlled through the ciment production line. This can be assessed by the following modulus: Lime saturation factor (**LSF**), the silica ratio (**SR**), the alumina modulus (**AM**) and the equivalent alkalis (**EA**).

1. Lime saturation factor (LSF)

Different formulas of LSF exist in the literature, all of them are based on the quaternary diagram $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Fe_2O_3$. The most used one is :

$$LSF=100*CaO/[(2.8*SiO_2)+(1.2*Al_2O_3+0.65*Fe_2O_3)].$$

This module gives information about the quality of the produced clinker and the degree of the burnability, it can also give an information on the alite and the presence of minor elements introduced by the use of alternative fuel or raw material, which highlights the necessity of a relation between LSF and the mineralogy of the clinker to fill the gap between the process and the product. The following relations have been established [7].

$$LSF=100*[(A+B*C3S)/(C+D*C3S)]$$

where the coefficients A, B, C and D are represented by the following:

$A=7.602*SR*(AM+1)+6.718*AM+1.429$

$B=(AM+1)*(SR+1)*0.01$

$C=[2.8*(AM+1)*SR+1.65*AM+0.35]*4.071$

$D=-[2.8*(AM+1)*SR+1.65*AM+0.35]*0.01$

This formula shows that the lime saturation factor is not a linear function of the alite amount. The application of this formula using the LSF versus mineralogy (alite) instead of chemistry appears to be more efficient in considering the presence of minor elements and their effect on the phase content [8].

2. The silica ratio (SR)

The SR determines the relationship between the solide and liquid phases in the clinker, it controls the burnability [9]. Its value should not exceed these limits [2.1 ; 3.4] in the raw meal. The SR ratio controls mainly the composition of clays and marls,i.e the higher the SR the higher the amount of silicate phases (alite and belite). The usual formula of the SR modulus is shown below

$SR=SiO_2/(Al_2O_3+Fe_2O_3)$

3. The alumina modulus (AM)

The AM as described in the following formula:

$AM=Al_2O_3/Fe_2O_3$.

It can determine the viscosity of the liquid phase during the clinkerisation. It ranges between 0.64 and 2.5. A high value of AM makes the alite training difficult which destroys the early strength of concrete.This modulus can be refined by adding a good iron ore [10].

As mentionned above all these modulus, the lime saturation factor (LSF) associated with the silica ratio (SR) and the alumina modulus (AM), are well known as a useful tool to design the raw meal of Portland cement clinker. In our work we are more focused on the silica ratio and the alumina modulus. Another modulus which can be useful in this study is the alkali equivalent.

4. Alkali equivalent (EA)

An alkali equivalent (EA) calculation, $EA=Na_2O+0.659\ K_2O$, seems necessary in order to prevent the penetration of alkalis (Na_2O, K_2O) into the body of the refractory bricks which reduces their durability. Furthermore, alkalis can also cause a massive ring formation, which can seriously restrict the movement of material and gas and lead to structure and composition changes in the refractories [11]. The EA defines the total alkalis converted into Na_2O. In some countries, Standards restrict the alkali equivalent up to 0.6 to prevent expansive reactions between the alkali and some aggregates in the concrete.

In this paper the aim is to perform an analytical program for clays and marls by X ray. This program allows to obtain a better management of the existing resources using the above mentioned modulus (LSF, AM, SR), allowing an easy assessement of the produced clinker quality.

EXPERIMENTAL SECTION

1. Samples preparation

The samples of marls and clays are firstly dryed in an oven at a suitable temperature of 110°C for 24 hours to eliminate the water and facilitate the grinding, then the particule size was reduced in a laboratory disc mill, by means of predominantly horizontal vibration, the material is ground by impact and friction and at the same time homogenized. The milled powder usually gives a zero refusal on a sieve of 60 microns after grinding. Finally the samples are kept in numbered holders and prepared for X-ray diffraction analysis, chemical analysis and X-ray fluorescence analysis.

The classification of the existing oxides of marls and clays is done according to their amonts, we have major, minor and trace elements (see Table I).

The determination of the loss on ignition (**LOI**) is a preliminary step before initiating the chemical analysis, it helps to classify the samples collected in two main groups clays and marls using the below classification.

Any chemical analysis of silicates starts with an appropriate disintegration of the matter and the dissolution of the attack result. Depending on the examined silicoaluminous materials, there's a significant difference in the choice of the means of attack which depends largely the success of the actual analysis [12]. For this reason two dissolution process are followed: the dry process and the wet one.

The dry process is used for the determination of the SiO_2, Al_2O_3, Fe_2O_3, CaO, and MgO amount. It is used when a silicate is not easily or hardly attacked by acids (especially hydrochloric acid (HCl)), it must be combined or calcined with an other body, forming a decomposable combination in contact with acid [13].

A description of the dry and the wet dissolution processes is assured in the following paragraph.

1.1. Dry process

0.5 g of each sample is introduced into a platinum crucible with 1-2g of $NaKCO_3$ added to facilitate the melting of sample. The whole is kept in the furnace at 1000°C for one hour, then the sample is immediately removed and kept into a desiccator to prevent the adsorption of moisture on the surface of the powder. After the crucible with the material is introduced into HCl/ H_2O solution. Heated to dry at 80°C the remaining material is mixed with10 mL of HCl (37%) and boiled for 15 to 20 minutes with the addition of the hot water, finally the solution is cooled under the hood and filtered with precision to minimize the losses.

This solution allows the determination of the amounts of aluminum (Al_2O_3), magnesium (MgO), iron (Fe_2O_3), calcium (CaO) by complexometric titration with EDTA while the residue will be used for the determination of SiO_2 amount by gravimetry [14].

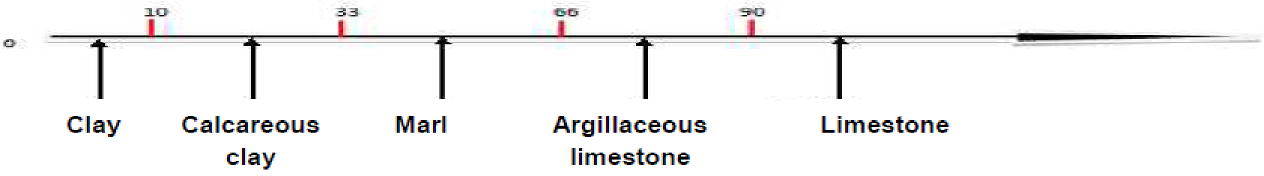
As mentioned above the dry process is performed using $NaKCO_3$, so the use of this method gives incorrect values of the % Na_2O and %K_2O, therefore another type of dissolution is needed: the wet process.

1.2. Wet process

0.25 g from each sample is introduced in a Teflon beaker with 5 mL of HNO_3, 5 mL of $HClO_4$ and 10 mL of HF and maintained on a heater plate at 150°C until dry. After we added 5 mL of $HClO_4$ and 20 drops of HCl the solution is filtrated, a part

Table I: Classification of oxides according to their content

Classification	Elements	Amount
Majors	Si(SiO_2), Al(Al_2O_3), Ca (CaO)	>10
Minors	MgO, Fe_2O_3, SO_3	0.5-10
Traces	Na_2O, K_2O	<0.5



of the filtrate is used for the determination of the amount of Al_2O_3, Fe_2O_3, CaO, MgO while the other part for the determination of %Na_2O et % K_2O by atomic absorption spectrometry. The other elements such as chloride and sulfates are determined respectively by Volhard's method and by gravimetry.

2. Techniques

The milled samples are pressed with a laboratory hydraulic press of 10 tons into briquettes for the XRD and XRF analysis, using a ARL 9900 diffractometer operating with CoKα radiation (λ=1.789). The samples were scanned from 2θ 8° to 80°. Step size is 0.03, the counting time is 1s per step. The tension was set at 40 kV and the current at 40 mA. The divergence slit was fixed at 1°, and the receiving slit was set at 0.0 mm. This instrument is equipped with a series of XRF fixed channels (monochromators), an XRF goniometer, and an XRD goniometer integrated in such a manner that both XRF and XRD measurements can be carried out on the same sample with the same tube conditions and under vacuum.

The determination of Na (Na_2O) and K (K_2O) present in the marls and clays is performed using a flame photometer installed at Bizerte cement laboratory.

$$\% Na_2O = -0,021 + 0.394 * ANa_2O$$

$$\% K_2O = -0.098 + 0.173 * AK_2O$$

The following formulas are the equations of straight calibration curves obtained by linear extrapolation (Beer-Lambert law) of couples of points (%, absorbance) measured on standard solutions.

RESULTS AND DISCUSSION

1. X-ray diffraction analysis

The mineralogical phases identification was carried out using the X'Pert HighScore Plus. A good interpretation of the diffractograms of clays and marls minerals requires a good knowledge of their structure to ensure the validity of the license model and the used parameters. The main mineralogical present phases are quartz (SiO_2), calcite, smectite, kolinite and dolomite. All samples have a similar mineralogical composition except the peaks intensity differs, we note the appearance of new reflection in the last sample it is contributed to $NaAlSi_3O_8$. The XRD analysis provides information about the mineralogical

Table II: Chemical analyses results of the sample A

Test number	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	CL	SO_3	LOI
1	44.55	14.68	7.34	5.11	5.92	0.026	0.66	0.042	0.264	16.82
2		15.14	7.18	6.08	5.23					
3		14.93	5.82	5.34	6.44					
4		15.59	7.2	5.53	6.58					17.82
5	44.7	13.56	7.02	5.42	6.5					
6		16.61	6.95	5.9	5.95					
7		16.62	7.98	5.91	5.57					16.32
8		16.62	8.46	4.7	6.49					
9	44.46	15.6	6.54	6.4	6.92					
Average	44.57	15.48	7.14	5.8	6.10	0.026	0.66	0.042	0.26	16.98
standard deviation	0.121	0.98	0.76	0.65	0.54	-	-	-	-	0.62

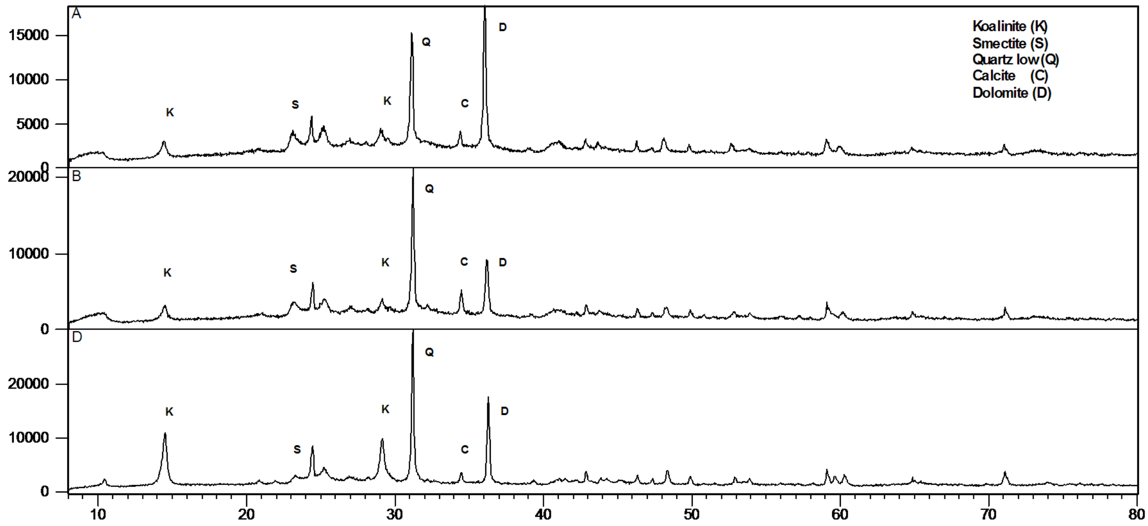


Figure : X-ray diffraction patterns of A,B and D samples

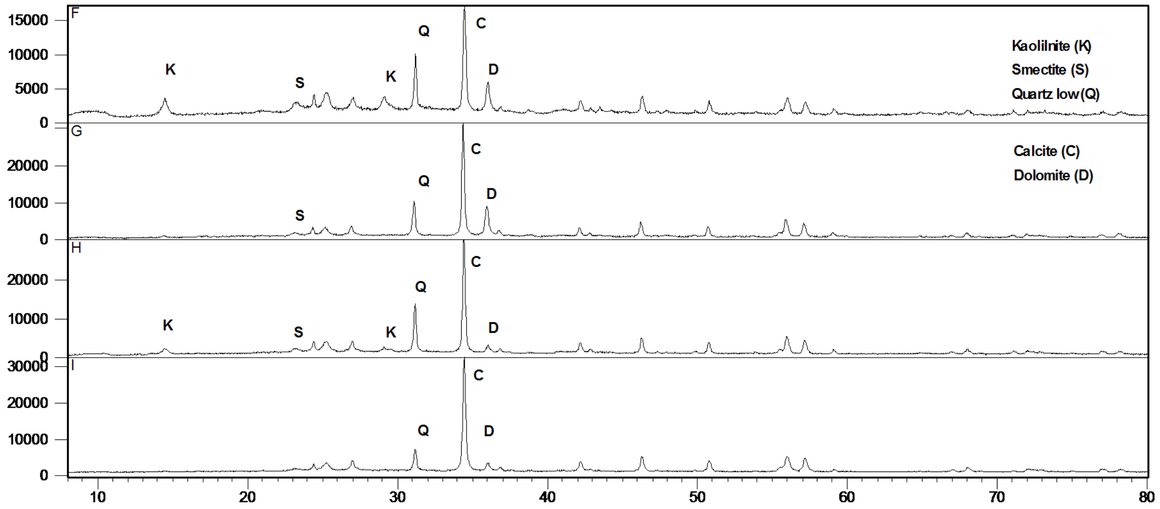


Figure : X-ray diffraction patterns of F,G H and I samples

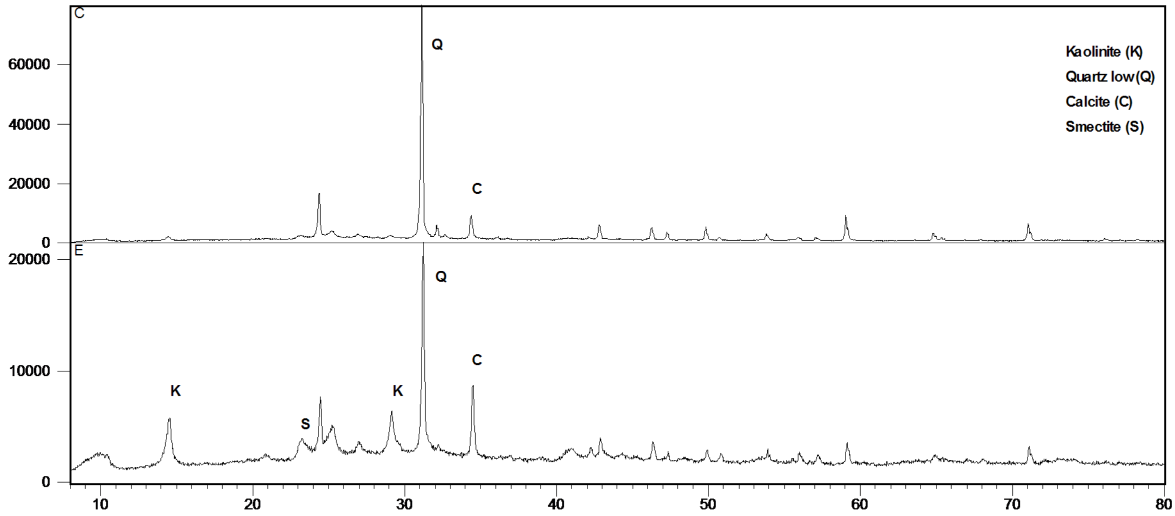


Figure : X-ray diffraction patterns of C and E samples

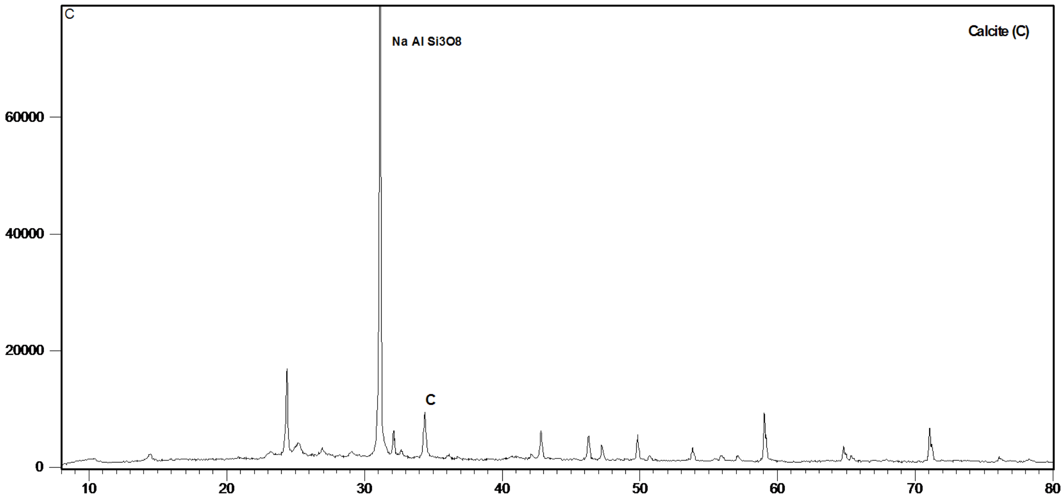


Figure : X-ray diffraction patterns of sample J

composition, so it informs about the chemical composition of samples which makes easy the choice of reactive and the samples dissolution.

2. Chemical analysis results

A serie of chemical analyses was performed on each sample in order to minimize the error and increase the fidelity of analysis.
The average of the analyses of each sample are summarized in table III, a calculation of the maximum and minimum is assured to determine the extent of the prepared range.

3. X-ray fluorescence analysis

To measure the X-ray intensity on the various elements a pellet was prepared for each sample and analyzed by X-ray fluorescence three times in order to have the average and standard deviation of three determinations (table IV).

Static given on the calculation of the average and standard deviation have shown an acceptable relative standard deviation except for Cl which recorded a value of 2.78. The average x-ray intensities of the analysed elements for marls and clays samples are summarized in the table V.

Table III: Chemical composition of samples

Samples	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Cl	SO_3	LOI
A	44.57	15.48	7.14	5.80	6.10	0.66	0.026	0.042	0.264	16.98
B	43.81	14.09	6.75	7.71	6.14	0.73	0.034	0.053	0.569	19.27
C	56.74	9.77	4.97	8.16	2.26	0.43	0.035	0.047	1.522	7.46
D	42.47	18.14	5.12	8.00	5.76	0.34	0.022	0.046	0.171	16.88
E	46.30	17.77	9.43	6.66	2.21	0.65	0.025	0.045	0.044	15.48
F	36.25	13.24	6.12	16.45	2.82	0.27	0.034	0.044	3.196	22.79
G	30.57	7.89	3.67	28.95	4.02	0.18	0.03	0.039	1.807	31.58
H	32.48	8.67	5.05	26.32	3.2	0.2	0.024	0.046	0.967	27.94
I	23.74	7.05	2.96	36.79	3.2	0.15	0.039	0.04	0.699	27.27
J	61.34	20.63	1.52	1.782	2.49	0.07	0.717	0.025	0.171	1.655
MAX	61.34	20.63	9.43	36.79	6.14	0.66	0.717	0.053	3.196	31.58
MIN	23.74	7.05	1.52	1.782	2.21	0 .07	0.02	0.025	0.044	1.655

Table IV: X-ray intensity of the sample A

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	Cl
Essay 1	272.448	109.403	466.864	85.852	40.820	1.953	74.315	1.486	0.383
Essay 2	271.541	109.015	465.403	85.764	40.698	1.971	74.144	1.527	0.401
Essay 3	271.380	109.072	465.676	85.811	40.590	1.980	74.078	1.519	0.403
Average	271.79	109.16	465.98	85.81	40.70	1.97	74.18	1.52	0.40
standard deviation	0.58	0.21	0.78	0.04	0.12	0.01	0.12	0.01	0.01
Relative standard deviation	0.21	0.19	0.17	0.05	0.28	0.70	0.16	0.37	2.78

These values will be used for the calibration curves determination of each element by linear regression based on the determination of the gradient a the order originally b and R correlation coefficient for the regression line. All curves presented an R> 0.97 will be accepted in cases of major elements for minors and trace elements R will be accepted from 0.94.

4. Tracing calibration curve

The treated samples are selected according to the amount of each chemical element quantified in order to have a range covering the variations of clay and marl suspected to be analyzed in Bizerte cement laboratory. These analyses will be used to prepare calibration curves to calibrate an ARL 9900 spectrometer. The calibration curves represent the variations of different oxides concentration already done by chemical analysis based on their relative intensities obtained by X-ray fluorescence intensities. It should cover different levels ranging from 0 to 100% for each assayed element but in front of the possible causes of error experienced by an X-ray spectrometry analysis system leaving very complicated the uncertainties determination requires users spectrometer to intersect the curve calibration of the instrument in several segments representing the tangent to the curve. The Figures 5, 6, 7 and 8 show the calibration curves of SiO_2 CaO Fe_2O_3 and K_2O.

5.The results of the calculated modulus

The established analytical program used to control the modulus: AM SR and EA in the raw

Table V: The average of X-rays intensities of the various elements analyzed for each sample

Samples	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	Cl
A	271.541	109.163	465.981	85.809	40.702	1.968	74.179	1.51	0.395
B	268.449	102.641	439.441	96.437	47.871	1.123	82.681	1.829	0.506
C	344.846	71.557	241.729	81.453	17.753	1.349	48.900	1.907	0.456
D	256.311	138.118	257.934	94.701	38.410	2.025	38.910	1.260	0.451
E	280.636	125.759	578.218	70.070	18.232	1.122	73.588	1.430	0.440
F	219.128	84.121	339.973	207.729	23.731	16.206	31.241	1.687	0.434
G	182.845	45.497	147.913	418.900	20.720	20.347	20.886	1.390	0.392
H	194.594	60.880	245.905	331.488	18.653	9.481	24.284	1.968	0.467
I	143.524	34.842	110.866	526.220	15.587	9.071	18.291	1.181	0.404
J	360.428	108.490	11.419	17.276	6.131	0.854	9.120	35.368	0.255

Table VI: The results of calculated modulus for the differents samples

Samples	AM	SR	EA
A	2.17	1.97	0.46
B	2.1	2.10	0.51
C	1.96	3.84	0.31
D	3.54	1.82	0.24
E	1.88	1.7	0.45
F	2.16	1.87	0.22
G	2.15	2.64	0.15
H	1.71	2. 36	0.15
I	2.83	2.73	0.14
J	13.57	2.77	0.76

powder. The modulus are calculated for the different studied marls and clays (see table VI).

The clay or marl fraction is usually controlled by the silica modulus which is generally desired between 2.1 and 2.8 in the following an SR examination.

SR<2.1

• AM> 1.6

The melting phase which based on alumina becomes highly viscous that is cause a casting during the Clinkerisation which usually accompanied with a decrease in the density of the melting phase and increase of the crustin thinness. As result the heat transfer from the flame to the ferrule increase and the refractory bricks become more stressed. Consequently the risk of cement kiln stop increase and the clinker will be like a slight drosses.

• 0.64 <AM <1.38

The liquid phase becomes very tacky and the crusting becomes very thick and dense. As result the crusting falls down accompanied by the tearing off the bricks. Furthermore the clinker will be on the form of large blocks that prevent the well functioning of the cooler and makes difficult the getting of the desired clinker.

SR>2.8

In this case the crystalline phase predominates the reactivity of the raw powder decrease which requires an increase in the heat capacity during the clinkerisation. The clinker becomes dusty forming a screen material which generally accompanied by

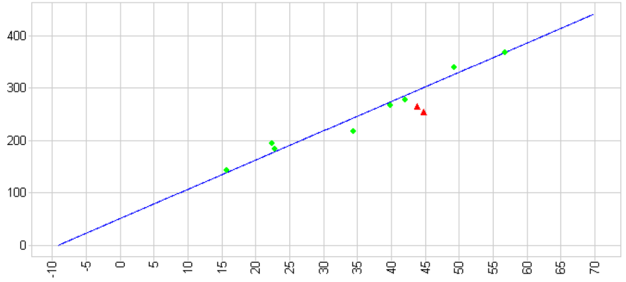


Figure 5: A calibration curve of SiO_2 in a series of clays and marls samples

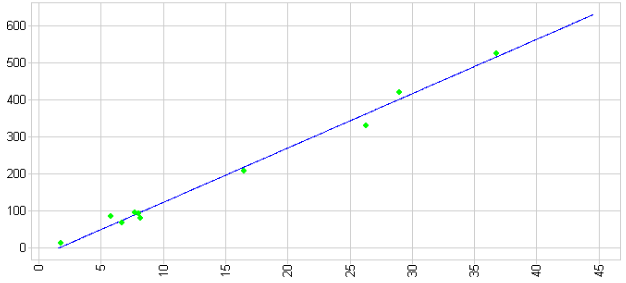


Figure 6: A calibration curve of CaO in a series of clays and marls samples

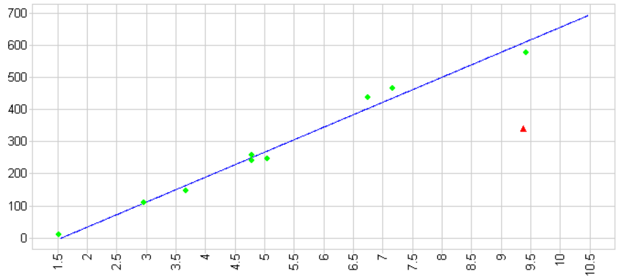


Figure 7: A calibration curve of Fe_2O_3 in a series of clays and marls samples.

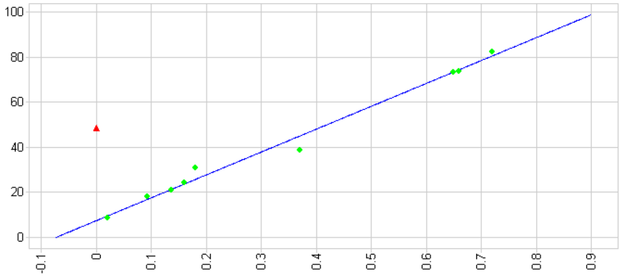


Figure 8: A calibration curve of K_2O in a series of clays and marls samples

a decrease in production further an increase in the specific fuel consumption.

The treated samples present a very variable silica modulus value extending from 1.70 to 3.84 to fix these values the cement factory usually use a correction elements which are mainly based on iron or alumina material. Regarding Bizerte cement factory the iron ore is added to lower the silica modulus thanks to its high content of Fe_2O_3.

For the alkali equivalent (EA) it represent an acceptable value exept for the last sample which define as a feldspath such as the main phase is $NaAlSi_3O_8$ which explain its highest value.

CONCLUSION

The program prepared can perform a lot of analyses in a few seconds that ‘s can save the lost time usually spent in the sample preparation phase and the chemical analysis. Furthermore all analyzes can be performed in better condition of repetability and reproducibility. Thanks to this program Bizerte Cement Factory has integrated an abandoned marls and preserved others to ensure the longevity of its quarries. Clays and marls represent the active part in the cement production regardless of the used limestone it will be the proper clay or marl and the necessary correction in order to maintain the good quality of cement.

REFERENCES

[1] A K. Chatterjee *Chemistry and engineering of the clinkerization process* - Incremental advances and lack of breakthroughs cement and concrete research 41(**2011**) 624-641.
[2] F. Sorrentino *Chemistry and engineering of the production process*: State of the art Cement and Concrete Research 41 (**2011**) 616–623.
[3] H.F.W. Taylor *Cement Chemistry Academic Press New York* **1990**.
[4] Michel Venuat, Michel Papadakis « *Contrôle et essais des ciments mortiers bétons* » 61 boulevard Saint-Germain- PARIS Ve **1961**.
[5] V. K. Klassen, E. P. Ermolenko, D.A. Michin and A. G. Novosyolov Problem of Impurity of Salts of Alkali Metals in Cement Raw Materials *Middle-East Journal of Scientific Research* 17 (8) (**2013**) 1130-1137.
[6] J. Nievoll, S. Jorg K.Dosinger and J. Corpus Sulfur Spurrite and Rings Always a Headache for the Cement Klin Operateur? RHI *Bulletin* **2007** pp.35-38.
[7] F. Sorrentino *Lime saturation factor new insight Cement Wapno Beton* 2 (**2008**) 82–88.
[8] F. Sorrentino *Modern Design of Raw Mix Proportioning of Portland Cement Clinker* to be Published at the 13th International Congress on the Chemistry of Cement Madrid, **2011**.
[9] Mohamed A. Aldieb Hesham G. Ibrahim Variation of feed chemical composition and it is effect on clinker formation - *Simulation process Proceedings of the world congres on engineering and computer science* **2011** Vol II.
[10] Nicholas Winter *Uderstanding cement* December **2012**.
[11] Hegde S. B.Chaturvedi S.**1995** *Effect of alkalis on alumina refractories in cement rotary kilns Refractories* 36 184-188.
[12] I.A.Voinovitch, J. Debras-Guedon et J. Louvrier *L'analyse des silicates* Paris **1962**.
[13] Dr Carl Friedheim et L.Gautier *Précis d'analyse chimique quantitative, les substances minerals*,Paris et Liége.
[14] The French standard CEN 196-2 published by the French Association of normalization "AFNOR"en **2006**.