XRF ANALYSIS OF PORTLAND CEMENT FOR MAJOR AND TRACE ELEMENTS.

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تحليل الأسمنت البورتلندي الرئيسية والضئيلة باستخدام الشعة السينية المفلورة.

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الملخص

يتم إنتاج الاسمنت البورتلندي الليبي في عدة مصانع محلية موزعة في عدة مناطق في ليبيا مثل مصنع لبدة، زليتن، سوق الخميس، درنه والفنتائح وغيرها من المصانع الاخري. تم أخذ العينات من هذه المصانع لغرض تحليل مكونات الاسمنت المحلي وذلك بتقدير المكونات الاساسية والضئيلة ومقارنتها بعينات اسمنت بورتلندي مستورد من اسبانيا، رومانيا، قبرص ومصر.في هذه الورقة تم استخدام منظومة الاشعة السينية المفلورة المتطورة (XRF) والمصنعة من قبل شركة (Spectro Xlab2000) الالمانية والمتكونة من انبوبة الاشعة السينية نوع (Rh) قدرتها 400W وتشتغل من 5-14kV، 13mA مزودة هذه المنظومة بكاشف نوع Si(Li) ذو الكفاءة العالية 148eV عند خط (MnK_{α}=5.9keV). ولضمان إثارة جميع نويدات او مكونات الاسمنت من Na حتي U في جزء من المليون (ppm) تم تزويد هذه المنظومة ب8 اهداف ثانوية. في هذه الورقة تم استخدام طريقة القرص المضغوط (pellet) وذلك بخلط 4g من الاسمنت الناعم مع 0.9g من الرابط (HWC) ويتم ضغطه الي 14tones . جميع التحاليل والقياسات الخلفية وغيرها يتم آلياً باستخدام برنامج (Xlab2000 pro). مقارنة نتائج XRF تمت مع نتائج جهاز الامتصاص الذري (AAS). من خلال النتائج المتحصل عليها تتضح أن المكونات

الكيميائية للاسمنت البورتلندي الليبي المصنع محليا يتقارب بعـــض الاحيـــان بالمواصـــفات الدولية للاسمنت البورتلندي.

ABSTRACT

Libyan portland cement produced in several factories around the country, in Liptis, Zleaten, Souq-Elkamis, Dernah and El-Fataeh, were analyzed for quantitative major and trace elements and mineral content, which were compaired with those imported from Spain, Romania, Cyprus, and Egypt. X-ray fluorescence Spectro Xlab 2000 spectrometer equiped with Rh-anod X-ray tube was used for the analysis of various samples. The detector Si(Li) with a resolution of 148 ev at Mn K_a= 5.9 Kev facilitates the determination of a wide range of elements from sodium to uranium, with a detection limit at sub ppm leveles. Cement samples in the powder form were analyzed using the pellet-technique. The pelletes were prepared by mixing 4g of the cement powder with 0.9g of binder (HWC) and pressed at high pressure. A full analysis including, background counting, matrix correction and all relevent corrections were achieved automatically by XLAB 2000 software package. For major and trace elements XRF results were higher for most of the elements than those analyzed with atomic absorption spectrometry. The mineral content shows that Libyan cement is comparable to the imported ones, also the Libyan cement meets the requirements of the international specifications of the portland cement.

KEYWORDS: ED. X-ray fluorescence, Cement.

INTRODUCTION

Portland cement is obtained by grinding and mixing materials such as clays, sheles and slates together with limestone and marl. These raw materials are then fed into a rotary cement kiln whose temperature reach up to 1480^{o}C. Where the raw materilas undergo complex chemical and physical changes required to enable them to react together through hydration. The first reaction is the calcining of limestone into lime (CaO) and carbon dioxide which occurs at about 900 ^{o}C.

$$CaCO_3 \longrightarrow CaO + CO_2$$

Dicalcium and tricalcium silicates (as well as small amonts of tricalcium aluminate and tetracalcium aluminoferite) are then formed by the bonding reaction of calcium oxides and silicates. These reactions occur while the components are in molten form. As the new compound cool, then is solidified into pellets called clinker. The clinker is then ground into a fine powder and a small amount of gypsum is added[1-3].

For portland cement, the chemical composition is controlled by the content of silica (SiO_2), lime (CaO), alumina (Al_2O_3), iron oxide (Fe_2O_3) and others. Table(1) shows the standard chemical composition of the portland cement. The oxides become characteristic clinker minerals which after the addition of gypsum will be ground to cement. Portland cement is made up of four main clinker compounds: Tricalcium silicate (allite) (C_3S), Dicalcium Silicate (belite) (C_2S), Tricalcium aluminate (C_3A), and Tetra-Calcium aluminoferrite (C_4AF), where C stands for calcium oxide, S for silica, A for alumina, and F for iron oxide. Small amounts of uncombined lime, magnesia, alkalis and minor amounts of other elements (titanium, manganese, etc.) are also present as indicated the standard mineralogical composition of portland cement is shown in table (2).

The chemical composition of cement influences its characterstics. The clinker mineral (C_3A) is the main clinker component for cement. The strength developed by portland cement depends on its composition of C_3S, C_2S, C_3A, C_4AF and the fineness (Blaine) to which it is grounded. The strength is measured by Mpa (N/mm^2) according to (ASTM and BS)[4,5]. The compressive strength is determined in different ways. For ASTM the strength is determined in accordance with ASTM–109, and for BS and other European countries, the strength is determined in accordance with EN196-1. Five types of portland cement are standardized in the U.S.(Standard Specification for portland Cement C 150-9); ordinary (Type I), modified (Type II), high-early strength (Type III), low-heat (Type IV), and sulfate-resisting (Type V). In other countries Type II omitted, and

Type III is called rapid-hardening. Type V is known in some European countries as Ferrari cement. Five types of portland cement are also standardized in the U.K .(Specification for portland cement BS 12; 1996); strength class 32.5N, 42.5N, 42.5R, 52.5N, and 62.5N. The different standard specification for portland cement contain different requirements of chemical and physical properties; MgO, SO3, alkalis as Na_2O, loss on ignition, insoluble residue, Boque composition, fineness (Blaine), soundness, autoclave expansion, compressive strength and initial and final setting.

TABLE (1). ASTM Specification of the Chemical Composition of Portland Cement[4].

Chemical Name	Common Name	Chemical Notation	Abbreviated Notation	Mass Contents %
Calcium Oxide	Lime	CaO	C	58-66
Silicon dioxide	Silica	SiO_2	S	18-26
Aluminium oxide	Lumina	Al_2O_3	A	4-12
Ferric Oxide	Iron	Fe_2O_3	F	1-6
Magnesium oxide	Magnesia	MgO	M	1-3
Sulphur trioxide	Sulphurican hyrite	SO_3	S	0.5-2.5
Alakaline Oxides	Alkalis	K_2O &NaO_2	K+N	<1

TABLE(2). ASTM Standard Mineralogical Composition of portland Cement[4].

Chemical Name	Common Name	Chemical Notation	Abbreviatd Notation	Mass Content %
Tricalcium silicate	Alite	$3CaOSiO_2$	C3S	38-60
Dicalcium silicate	Belite	$2CaOSiO_2$	C2S	15-38
Tricalcium aluminate	Belite	$3CaOAl_2O_3$	C3A	4-12
Tetracalcium aliminoferite	Celite	$4CaOAl_2O_3$ Fe_2O_3	C4AF	10-18
Pentaclcium trialuminate	Celite	$5CaO_3Al_2O_3$	C4AF	1-3
Calciumsulphate dihyrate	gypsum	$CaSO_4.2H_2O$	CSH2	2-5

The first objectivs of the present work are to use XRF for the determination of the major and trace elements in the libyan and imported portland cement. The second objective are to compare the results which obtained by XRF with those obtain by the AAS and with standard specification of Portland cements.

EXPERIMENTAL.

APPARATUS AND CHEMICALS.

Energy Dispersive X-ray Fluorescence(EDXRF) Spectrometry has been in use for nearly 20 years. The EDXRF technique is rapid and non-destructive to the sample, safer for the opeator, and there are no additional waste streams generated during the analytical process. All the measurements of pressed powder pellet technique, were performed with the Spectro XLAB 2000 spectrometer in the follwing configuration, 400W Rh-end 250mm Be window X-ray tube with the intergrated oil cooling system, Mo secondary target for the excitation of the elements (Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Rb, Sr, Y, W,Hg, Pb, Bi), Al_2O_3 scatter for the excitation of elements (Mo, Ag, Cd, In, Sn, Sb, I, Ba, La), and HOPG-polarization crystal for the excitation of the elements (Al, Si, P, S, Cl, K, Ca, Ti, V). A silicon-lithium detector Si(Li) with resoulation of 148eV, related of the MnK_α line and account rate of 10000cps coupled to simultaneous detection of fluorescence radiation in 4000 channels (multi-channel), ranging from 0.4-50keV and PC computer, where the peak areas were calculated using comericaly XLAB2000 software package.

Atomic absorption spectrophotometer AA-6601F from Shimadzu equiped with flame burnner and HCL from Hamamatsu was used for determination of elements in the ppm range, while AA-6701F equiped with GFA 6500 graphite furnace and ASC 6000 autosampler from Shimadzu was used for the determination of elements in the sub ppm range. Flame Photometer Jenway Pep 7 was used for the determination of K and Na while all others were determined with AAS.

For the preparation of standrads of different elements, 1000 ppm stock standared solutions from Merek were used, and deionized water from ELGA Maxima ultrapure water unit was used for the preparation of samples and the dilution of the standards. Analytical grade acids were used for the digstion of the samples.

PREPARATION OF SAMPLES FOR MEASUREMENTS.

Five portland cement samples were collected from differnet locally cement factors Lipits, Zleatin, Dernah, El-fateah and Soq El-Kamiss, and four imported cement samples from Spain, Romania, Cyprus and Egypt were analysed by pellet method[7-11]. In this method 4.0g sample of the pulverized portland cement material (<40μm) were mixed with 0.9g Hoechst-Wax micropowder C (HWC) as a binder in agate mortar, and pressed into pellets with a diameter of 32mm. The accuracy of the measurementes is improved by increasing measuring time. As a routine check of the analytical method, the certified reference materials[12-15] such as Soil-7(IAEA), SL-1(IAEA), V9(IAEA) for powder method, while certified reference materials such as GnA, G-2, AVG-1, G-2 and BIR-1 were used for pressed powder pellet techniques.

In every routine analytical run, one sample is chosen at random for every 20 samples and analysed in duplicate. This provides a measure of the reproducibilty and precision or the analytical procedure using standard samples as mentioned above, where the results of the selected elements related to main elements of portland cements, are summarized in Table 3. Machine drift was monitored and corrected by the routine running of a commercial monitor sample (GnA) containing approperiate levels of elements of interest.

Table(3).Concentration (%) of selected elementes in standard samples using pellet technique.

Element	W-2		G-2	
	Certified	Average±s.d	Certified	Average±s.d
Na	1.587	2.732±0.532	3.027	4.485±0.280
Mg	3.842	3.723±0.065	0.452	0.565±0.027
Al	8.124	10.015±0.102	8.140	8.663±0.068
Si	24.513	28.567±0.235	32.291	36.730±0.35
S	0.008	0.001±0.000	0.010	0.00±0.01
K	0.523	0.581±0.017	3.719	4.017±0.037
Ca	7.768	8.282±0.083	1.401	1.500±0.021
Fe	7.594	7.605±0.097	1.881	1.809±0.020

The accuracy is estimated by analysis of a well characterised in-house sample of composition most closely approximating the unkown. Analytical precision varies from element to element as does detection limit but generally the major oxides have a detection limit of 0.01% and a relative accuracy of 0.5% by the pressed powder pellet technique.

For AAS analysis, the samples were grinded, then digested with hydrochloric-nitric acid mixture. For the digestion 0.2-0.5 g sample was wieghted in 250 ml beaker, 12.5 ml deionized water, and 12.5 ml 37% HCl were added and heated on a hot plate near dryness, then 2.5 ml of 65% HNO_3 is added and heated near dryness. The contents were transferred to 50 ml volumetric flask and completed to the mark with deionized water, now the sample is ready for analysis by AAS.

For the determination of different elements by AAS several atomization techniques were used. For the determination of Ca, Cd, Co, Cr, Cu, Fe, Mg, Ni, and Zn Air-Acetylen flame was used, while Nitrous Oxide-Acetylen flame was used for Al, Ba, and Mo. For the determination of Pb, and V Graphite Furnace was used. For the determination of K, Na flame Photometer was used.

RESULTS AND DISCUSSION.

XRF and AAS results of Libyan produced portland cement for the major elements in five factories are listed in Table(4), while Table(5) show the results of the imported Portland cement. Form the XRF results of Libyan cement samples, shows a little high of CaO content than the ASTM specification of the chemical composition of Portland cement, except that results from Dernah which are within the range of ASTM specification. The samples from Liptis, Zleatin and Soq El-Kamiss a limit but generally the major oxides have a detection limit of 0.01% and a relative accuracy of 0.5% by the pressed powder pellet technique.

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Table 5 shows the resuls of the chemical composition of the imported portland cement samples. All samples have a little high CaO and all have high SO_3 content. For the Spain cement the content of all the oxides is lower than the specification except CaO which is within the range. The Rromanian cement has oxides content within the range of the specification except for SO_3 and the akali oxides which are a little higher.

Table(6) shows the results of the concentration of major elements in Libyan cemeant analyzed by XRF and AAS. While the result of the imported one are shown in Table(7). The XRF results for most of the elements are higher than those analyzed by AAS for most of the samples. Some samples (Dernah, SoqElkamis, and all imported ones) showed higher AAS results for Ca content. Sample from Egypt, showed higher Mg for AAS results. For Fe the results with the two techniques are in good agreement. In general XRF showed better precision.

The results of trace elements in Portland Cemect analyzed by XRF and AAS for the localy produced are presented in Table 8, and for imported are in Table 9. As can seen from the results, all XRF results are higher than AAS results except for Cu which showed good agreement of the two methods, only in two cases (Alfataeh and Dernah) showed little higher values, and for Mo AAS results are higher for SoqElkamis and Lipts samples, also for V Lipts AAS results is higher than XRF result. For the imported samples, Cu concentration determined by AAS are lower than those determined by XRF, also for other trace elements except for Mo for which AAS results are higher than XRF results with the exception iof the Cypruss one.

TABLE (4). Chemical composition of locally produced cements analyzed by XRF(in %).

Oxides	Lipits	Zleatin	Dernah	EL-fataeh	Soq Al-Kamis
CaO	71.49±0.21	71.43±0.21	61.81±0.18	71.94±0.22	69.33±0.20
SiO_2	30.17±0.12	29.72±0.12	25.96±0.10	26.71±0.11	27.99±0.11
Al_2O_3	5.37±0.07	5.29±0.07	7.41±0.08	6.31±0.08	4.29±0.06
Fe_2O_3	3.39±0.02	2.98±0.02	1.86±0.01	2.75±0.02	3.67±0.02
MgO	2.37±0.12	2.50±0.12	3.15±0.12	1.80±0.11	2.31±0.11
SO_3	4.20±0.02	4.36±0.02	3.59±0.02	5.16±0.02	1.74±0.01
Na_2O	0.61±0.01	0.62±0.01	0.50±0.02	0.63±0.01	0.55±0.01
K_2O	0.59±0.13	0.72±0.02	0.65±0.23	0.94±0.15	1.06±0.24

TABLE(5). Chemical composition of imported produced cemnets analyzed by XRF(in %).

Oxides	Spain	Romania	Cyprus	Egypit
CaO	68.63±0.20	65.76±0.20	58.226±1.77	68.94±0.21
SiO_2	17.99±0.08	24.03±0.10	29.15±0.83	22.55±0.10
Al_2O_3	1.94±0.04	4.70±0.06	6.143±0.15	5.29±0.06
Fe_2O_3	0.18±0.01	3.69±0.02	2.766±0.04	3.69±0.02
MgO	0.49±0.07	2.30±0.11	3.240±0.06	0.67±0.09
SO_3	3.31±0.01	3.91±0.02	3.458±0.10	4.72±0.02
Na_2O	0.52±0.01	0.58±0.01	1.082±0.03	0.59±0.02
K_2O	0.43±0.32	1.69±0.54	<0.523	0.05±0.36

TABLE(6). Major elements in Libyan portland Cement Determined by XRF and AAS,(in %) .

El.	SoqAlkamis	Al-Ftaeh	Dernah	Zleaten	Lipts
Ca	46.12±0.57	51.06±0.50	44.18±0.13	51.39±0.34	48.50±0.30
	46.69±0.87	48.69±0.43	51.96±10.06	44.28±1.23	42.83±4.7
Al	2.28±0.007	3.32±0.02	3.92±0.04	2.84±0.04	2.47±0.03
	0.80±0.003	1.17±0.04	1.16±0.13	0.95±0.03	0.92±0.04
Si	13.29±0.21	12.16±0.12	9.70±0.42	14.02±0.13	11.07±0.12
Fe	2.60±0.03	1.91±0.02	1.30±0.01	2.10±0.01	2.88±.03
	2.67±0.005	2.32±0.03	2.34±0.36	2.18±0.01	2.29±0.14
Mg	1.42±0.03	1.09±0.004	0.88±0.05	1.51±0.01	1.65±0.02
	0.86±0.002	0.74±0.02	0.73±0.06	0.71±0.02	0.94±0.08
K	0.88±0.02	0.79±0.007	0.61±0.03	0.60±0.03	0.43±0.04
	0.43±0.01	0.43±0.001	0.44±0.07	0.28±0.04	0.30±0.02
Na	0.37±0.005	0.47±0.0	0.39±0.02	0.46±0.0	0.42±0.005
	0.08±0.005	0.25±0.02	0.23±0.04	0.19±0.06	0.13±0.014
S	0.66±0.003	2.07±0.01	1.44±0.006	1.70±0.007	1.66±0.006

TABLE(7). Major elements in imported portland cement determined by XRF and AAS. (in %).

Element	Egypt	Romania	Cyprus	Spain
Ca	49.54±0.27	46.70±0.30	41.61±1.27	49.31±0.22
	49.89±2.47	47.31±0.08	44.54±0.82	51.47±0.89
Al	2.77±0.06	2.46±0.03	3.25±0.07	1.04±0.04
	1.22±0.006	0.93±0.04	1.38±0.007	0.48±0.02
Si	10.42±0.17	11.15±0.08	13.63±0.39	8.56±0.22
Fe	2.55±0.04	2.58±0.006	1.93±0.02	0.13±0.001
	3.04±0.02	2.57±0.03	1.99±0.01	0.17±0.01
Mg	0.41±0.006	1.27±0.11	1.95±0.03	0.29±0.006
	0.44±0.01	0.79±0.02	0.13±0.004	0.23±0.01
K	0.04±0.0005	1.40±0.06	0.90±0.03	0.36±0.04
	0.11±0.005	0.44±0.004	0.42±0.05	0.24±0.002
Na	0.44±0.005	0.42±0.005	0.39±0.01	0.39±0.0
	0.28±0.0	0.11±0.004	0.18±0.04	0.11±0.004
S	1.92±0.002	1.56±0.006	1.35±0.004	1.34±0.01

TABLE 8: Trace elements in Libyan portland Cement determined by XRF and AAS. (in ppm)

El.	SouqAlka	Alfataeh	Dernah	Zleaten	Lipts
Cu	5.75±0.65	4.67±0.33	6.22±1.0	4.4±0.20	4.55±0.05
	5.46±0.17	8.37±0.07	7.29±1.33	4.69±0.60	4.04±0.48
Zn	35.30±2.9	46.10±0.75	15805±5	49.05±2.95	40.70±2.30
	9.93±0.94	24.31±0.20	24.28±3.94	24.67±0.55	21.92±2.63
Co	56.0±15	51.0±0.82	44.67±2.87	51.50±0.5	56.50±0.5
	13.26±1.2	14.07±1.38	9.13±0.71	11.69±0.9	12.52±2.4
Ni	19.80±3.0	18.30±1.18	84.60±6.1	9.75±0.65	17.80±5.8
	16.44±0.1	15.88±0.66	20.40±6.64	6.63±0.94	11.45±0.53
Cr	185.0±23	101.5±1.5	2918.5±14.5	115.0±20	158.5±23
	39.11±1.2	81.42±1.49	99.47±12.28	67.21±0.5	33.75±0.53
Cd	1.70±0.10	3.30±0.2	3.8±0.8	5.3±0.4	2.3±0.6
	0.05±0.06	0.30±0.09	0.30±0.12	0.05±0.04	0.103±0.09
Mo	4.35±0.15	4.33±0.05	3.73±0.17	4.8±0.6	3.7±0.1
	8.81±0.17	2.71±1.37	Nd	4.27±0.3	4.57±1.93
V	73.0±16.9	89.0±1.0	134.0±3.7	90.0±4.0	95.5±0.5
	39.23±11.	48.98±4.13	57.23±11.36	58.21±3.3	102.07±0.4

TABLE(9). Trace elements in imported portland cement determined by XRF and AAS (in ppm).

El.	Egypit	Romania	Cyprus	Spain
Cu	5.67±0.21	150.0±8.0	101.0±0.2	<3.35
	4.24±0.17	76.87±0.4	83.32±0.37	2.34±0.17
Zn	56.2±3.4	308.4±8.1	155.7±5.7	11.4±0.4
	29.72±0.68	181.66±3.15	31.41±0.17	6.61±0.32
Co	60.67±0.47	233.0±34	235±26	<15.0
	17.82±1.67	15.86±0.49	36.79±0.8	8.31±1.01
Ni	32.3±6.7	62.5±9.4	54.4±7.9	44.4±3.4
	22.31±0.63	38.89±2.5	23.18±1.56	42.15±0.77
Cr	137.7±8.3	260.0±34	244.0±29	120±7
	69.74±3.77	47.85±0.68	54.95±0.88	17.25±1.05
Cd	3.0±0.6	10.85±0.85	7.4±0.30	<1.30
	0.081±0.017	0.90±0.018	0.11±0.003	0.27±0.04
Mo	4.2±0.3	5.95±8	5.15±0.25	<3.0
	7.46±0.37	9.22±0.95	4.74±0.84	11.72±1.93
V	95.0±1.0	107.0±11.0	98.0±1.63	152.5±2.5
	25.59±9.01	58.73±2.25	18.96±0.36	17.17±0.97

Ca	X-Ray Spectrometry (XRF)
	Atomic Absorption Spectrometr (AAS)

CONCLUSION.

In general, an X-ray flouresecence is an accepted technique for analyzing cement and other material in the cement processing, where the pellet technique used in this work provides good accuracy, precision, and strongly depends on the element of interest. It is important to note that pellet technique is not ideal for some of the major elements, where the precision is good, but the accuracy is not compared with fused glass disc method. Also the results meets or exceed ASTM qualification specification, and finaly there is a good agreement between AAS and XRF results for trace elements.

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