Chemical Composition and Heavy Metal Content of Portland Cement in Northern Tunisia

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ABSTRACT: *This study aims to determine the major elements of Portland cement type I and II (CEMI and CEMII) in a cement factory in north Tunisia and which metal elements are introduced into the production process. We determine also the metal input rate and their distribution at the entrance and exit of the process. The major elements were analyzed and the trace elements (Arsenic, barium, lead, mercury, boron, strontium, Cadmium, Chromium, copper, manganese, nickel and zinc) were identified. The concentrations of heavy metals in CEMI showed no significant difference $p<0.05$ with those in CEMII. All refractory metals generally tend to be incorporated into the clinker (Ba, Sr, Mn, Ni, Cu, Zn, Cr and V), while the lower part, especially volatile and semi volatile metals accumulates in the cement dust. Most metals in cement are infused with clinker. Heavy metals in the cement can originate from a variety of process in cement manufacture, including its initial presence in raw materials and fuel, incorporation into kiln refractory brick, metal erosion from the raw mill grinding process, and in other forms such as gypsum, and cement kiln dust.*

KEYWORDS: *Portland cement; Heavy metals; Raw materials; Clinker; Cement kiln dust; Environmental auditing.*

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INTRODUCTION

Cement is an essential material for building and civil engineering construction that affects the environment during production and consumption process. Heavy metals are the major hazard elements presented in the cement. These toxic elements originate mainly from the raw materials, but also from refractory bricks lining the kiln, mineral inputs or the grinding media (normally high-chromium white cast iron) in the final finishing mills [1]. The trace element content of clinker is of high scientific interest and can be used to solve practical problems, too, for example, to determine the origin of the manufacturing works. The first paper on a similar topic was published in 1993 by Goguel and StJohn [2], showing the Ba, Sr and Mn concentration of Portland cements in New Zealand concretes. The trace element content of cements can be used to identify the manufacturing factory and to determine the origin of the Portland cement. This work will examine the trace element content of cement produced in northern Tunisia.

The Cement Factory of North of Tunisia currently produces the following hydraulic binders: Artificial Portland cements (standard I): CEM I 32.5 and CEM I 42.5 according to the European standards corresponding respectively to the CP I 32.5 and CP I 42.5 according to Tunisian standard NT 47.01-92. Portland cement is made of; limestone CEM II A-L 32.5 according to the European standard corresponding to the CP with limestone II Al 32.5 according to Tunisian standard NT 47.01-92.The artificial lime CHA. 10 according to Tunisian Standards NT 47-02.

Portland cement is used in the construction industry as a binder in concrete. The basic raw materials of Portland cement are lime (CaO), silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3). Cement is produced in two steps: in the first step, cement clinker is produced from raw materials. In the second step cement is produced from the cement clinker. In the manufacturing process, the clinker is crushed, then ground to a fineness for the desired composition and then heated up to 1400–1600 °C. The amount of gypsum added ($CaSO_44H_2O$) controls the setting time of the cement. The resulting product consists of tricalcium silicate (3CaO SiO_2), dicalcium silicate ($2CaOSiO_2$), tricalcium aluminate ($3CaOAl_2O_3$) and tetracalcium alumino ferrite ($4CaOAl_2O_3Fe_2O_3$) [3]. Cement production has several quite serious environmental hazards associated with it, including dust emissions and contaminated run-off water. Since cement production is energy intensive, it has a number of environmental effects, including greenhouse gas emissions, air pollutants such as SO_2, NOx, CO and heavy metals [4]. The negative environmental impacts are also associated with the used fuels in cement manufacture.

The cement industry requires analysis of major elements % including Si, Ca, Al, Fe and S and also minor elements such as Na, K, Ti, Mg, P, Mn. The trace elements including Cr, Pb, Zn, Ni, As, Cd, V and Cu, are also very important for environmental pollution control, which are present at ppm levels. This study focuses on the toxic substances produced by cement manufacture, with a specific focus on heavy metals. Our investigation aims also to determine the introduced metal elements into the production process of Portland cement, the metal input rate and their distribution at the entrance and exit of the process.

EXPERIMENTAL SECTION

Chemicals, reagents and glassware

All chemicals and reagents were of analytical grade and all standards were prepared from reagent grade chemicals (Perkin Elmer Pure – Atomic Spectroscopy Standard). All glassware was rinsed successively with detergent and distilled water three times prior to use.

Sampling

In experimental researches, data, which include analysis of trace element from raw materials to products, were collected from cement Factory in north Tunisia in April 2015.

Cement factory in northern Tunisia produces two types of cement (1) Portland cement " CEM I 42.5 N ", (2) Portland cement: CEM II A-L 32.5 N conform following standards. The more detailed characteristics of studied cement composition are in Table 1.

The materials used in this study in addition of cement sample included the following:

(3) Gypsum, (4) Clinker (5) Limestone, (6) Marl, (7) iron ore (8) Kiln dust

The chemical composition and specific surface area (Blaine) SSB:

The mineral contents of the cements were calculated based on Bogue's formula as outline by [6].

Table 1: Composition of studied samples.

	CEMI	CEMII
Clinker %	95	80
Calcareous %	5	20

$C3S = 4.07CaO - 7.6024\ SiO_2 – 6.7187\ Al_2O_3 – 1.4297\ Fe_2O_3$

$C2S = -3.07CaO + 8.6024\ SiO_2 + 5.0683\ Al_2O_3 + 1.08\ Fe_2O_3$

$C3A = 2.6504\ Al_2O_3 – 1.692\ Fe_2O_3$

$C4AF = 3.0432\ Fe_2O_3$

The Bogue calculation is a means of estimating the amount of the dominant minerals available in cement, based on its oxide composition. The potential phase compositions is important in assessing cement properties of [7].

The basic chemical composition of tested samples were investigated by X-Ray Fluorescence (XRF) analysis [8]. The chemical compositions were performed with the X-Ray Fluorescence (XRF). The XRF machine uses a polarized energy dispersion. About 4 g of the cement sample was mixed with about 0.09 g of wax. The mixture was milled in a milling machine for about three minutes to produce a homogeneous mixture, obtaining a particle size of about 60 μm. The mixture was placed in a die and compressed under the press pellet equipment. The equipment produced a pellet and which was then placed in the XRF. The chemical analysis of each sample were performed three times [9]. Phase composition for cements CEMI and CEMII estimates by X-ray powder diffraction and Rietveld analysis are becoming more widely used in the cement industry. Blaine specific surface tests by using of NF P 94-054 and NF EN 196-6 respectively, where each recorded result was the average value of three successive measures.

Experimental Procedure for the determination of Heavy Metals concentration

Triplicate subsamples of approximately 1 g of well homogenized solid samples were accurately weighed on an analytical balance, drying and sieving of sample on the grain size < 2 mm. Heavy metal concentration including As, Br, Pb, Hg, Ba, Sr, Cd, Cr, Cu, Mn, Ni and Zn were measured using an ICP-OES-AS Inductively Coupled Plasma Optical Emission Spectrometry". CZ_SOP_D06_02_001 (US EPA 200.7, ISO 11885, samples prepared as per CZ_SOP_D06_02_J02 chap. 10.3 to 10.16,10.17.5, 10.17.6, 10.17.9 to 10.17.14) Determination of elements by atomic emission spectrometry with inductively coupled plasma and stoichiometric calculations of compounds concentration from measured values. Sample was homogenized and mineralized by aqua regia prior to analysis. The results were expressed in mg/Kg. Data presented are average of three replications.

RESULTS AND DISCUSSION

The chemical composition of Portland cement

Chemical composition showed difference between tested materials (Fig. 1). CaO followed by SiO_2, Al_2O_3, and $Fe_2\ O_3$ are the predominant oxide of limestone. The minor oxides include MgO, K_2O, and SO_3. Limestone contains also impurities of SiO_2, Al_2O_3, $Fe_2\ O_3$, MgO, alkali, etc. SiO_2, Al_2O_3, Fe_2O_3 of these ingredients are the main components that make up cement mineral.

The predominant oxide of marl were SiO_2, followed by CaO, Al_2O_3, and $Fe_2\ O_3$. The minor oxides include MgO, SO_3 and K_2O. Marls are an excellent raw material for cement manufacture, because they contain the lime and the clay component in an already homogenized condition.

The predominant oxide of iron ore were Fe_2O_3 followed by SiO_2, Al_2O_3, and then CaO.

The predominant oxide clinker were CaO followed by SiO_2, $Al_2\ O_3$, and then $Fe_2\ O_3$ and the minor oxides include MgO, K_2O, SO_3 and Na_2O. To control setting time effectively, cement needs a minimum amount of calcium sulfate, mostly in the form of gypsum added to the clinker.

The chemical composition of Portland cement involves both major and minor oxides [10]. The major oxides include CaO, SiO_2, Al_2O_3, and $Fe_2\ O_3$ whereas the minor oxides include MgO, SO_3, and some alkali oxides (K_2O and Na_2O) and sometimes the inclusion of other compounds, $P_2\ O_5$, Cl, Ti O_2, Mn O_3 [10]. The Portland cement CEM is a powdery substance made from clinker and gypsum; the basic components of tested cement samples measured by XRF spectroscopy expressed in form of oxides in weight % are presented in Table 2.

The Portland cement was analysed by XRD, both CEMI and CEMII (Fig. 2 and Fig. 3) X-ray powder diffraction analyses include triplicate scans of each sample treatment (cement CEMI and CEMII). There are several

Table 2: The chemical and specific surface area (Blaine) of Portland cement.

	CEMI	CEMII
SiO_2 %	18.23	18.73
Al_2O_3%	3.89	3.96
Fe_2O_3 %	3.57	3.7
CaO %	60.95	59.97
Mg O %	1.27	1.31
K_2O %	0.48	0.47
SO_3 %	2.75	2.85
Na_2O %	0.51	0.403
Specific surface (m^2/kg)	389	354

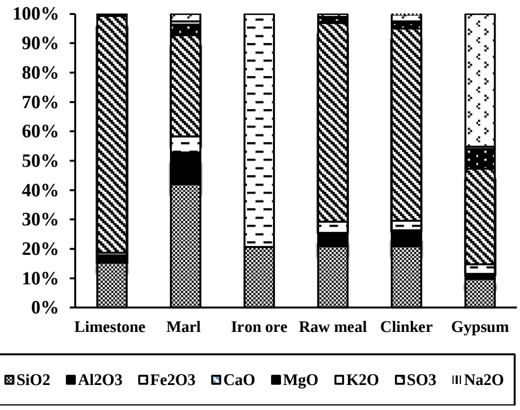

Fig. 1: The chemical composition of studied sample.

methods which may be used to determine the phase and phase composition of the cement. X-ray powder diffraction method is highly suitable for both qualitative and quantitative phase analyses of cement and clinker. The elemental composition of cement is usually determined by X-Ray Fluorescence (XRF) method.

An initial comparison of the peak intensities between cements provides some insights on their relative compositions. The effects of concentrating specific phase groups is seen by the increased peak intensities in the extraction residue patterns as well as the improved clarity of the simpler residue mixture.

The four major components of Portland cement are alite (C_3S–Ca_3SiO_5), belite (C_2S–Ca_2SiO_4), aluminate (C_3A–$Ca_3Al_2O_6$), and aluminoferrite (C_4AF). While the minor components are gypsum, calcium, sulphate and hemihydrate. Each of the major components, in turn, can exist in several polymorphic phases (Fig.2 and Fig.3).

The monoclinic phase of "alite" C_3S has a major characteristic peak at $2\theta = 32°$. The β-C_2S phase has a medium strong peak at 41.28° which although has some overlap with alite phase. Alite phase in cement and in cement hydration products and also to determine the degree of hydration of cement when an internal standard is used with cement reaction products. The major peaks of C_4AF, cubic and orthorhombic C_3A lie in the range 32° to 34°, it is very difficult to identify these phases separately in cement.

The Portland cement CEMI and CEMII have relatively high aluminate content and relatively low ferrite content. The XRD pattern of CEM showed alite and balite present as the main phases.

A comparison with each cement brand indicated variations in the chemical compositions existing between them. The predominant oxide compositions were CaO followed by SiO_2, Al_2O_3, and then Fe_2O_3 in that order. The minor oxides included MgO, Na_2O, K_2O, MnO, TiO_2, P_2O_5 and SO_3 (Table 2).

The amount of SiO_2 in Portland cement within the range 18% to 19%.The cement CEM I have slightly lower silica than the CEMII 18.23 and 18.73 respectively. The variation of aluminum oxide was found that amount of Al_2O_3 in the studied samples is lower than 4.00% On the other hand the iron Fe_2O_3 contentin in the cement samples within the range 3% to 4%. Amount of CaO within the range 60% to 61%. cements have same MgO 1.27 and 1.31% respectively. The magnesia content is not to exceed 2% because higher magnesia contents may be detrimental to the soundness of the cement, especially at late ages.

The amount of SO_3 in Portland cement 2.75-2.85 %. The cement CEMI has lower content of Sulfuric anhydride

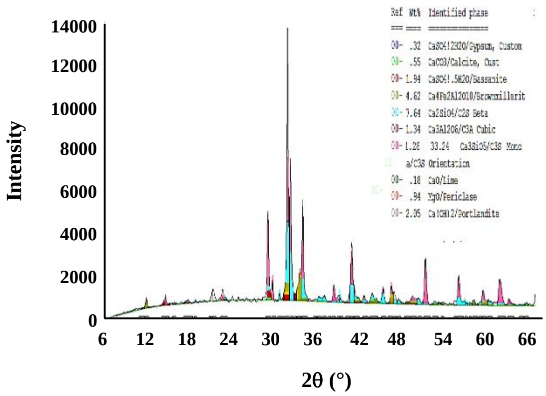

Fig. 2: X-ray Powder diffraction Portland cement I.

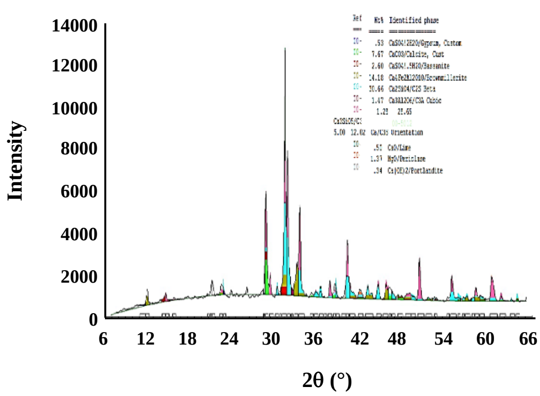

Fig. 3: X-ray Powder diffraction Portland cement II.

2.75%. High percentage of SO3 tends to cause unsoundness of cement. Portland cement contains usually around 5% of gypsum, but its level from SO3 must be less than 4%, according to the European standard EN 197-1. The resulting value, of the (SSB) of Portland cement CEMI (389) and CEMII (354 m^2 /kg). The analysis of each type of cement shows that the SSB <5000. A better parameter for describing the fineness of the cement is the specific surface area. Because most of the surface area comes from the smallest particles. The most common method for characterizing the surface area of a cement is the Blaine air permeability test. The chemical composition of investigated cement samples correlate to the standard chemical composition of particular cement types [11]. The difference in the basic components percentage for tested 126 A. cement types depends on their composition. CEM I cement consists mainly of clinker. Other studied cement types include various other components such as blast furnace slag pozzolana or fly ash. Four major compounds in Portland cement are C2S (dicalcium silicate), C3S (tricalcium silicate), C_3A (calcium aluminate, and C_4AF(tetracalcium aluminoferrite). These four compounds are formed by burning reaction of CaO, SiO_2, Al_2O_3 and Fe_2O_3 components at high temperature. The silicates, C_3S and C_2S, are the most important compounds, which are responsible for the strength of hydrated cement paste. The presence of C_3A in cement is undesirable. C_4AF is also present in cement in small quantities, and, compared with the other three it does not affect the behavior of the cement significantly. The SiO_2 content for all the samples is in the range of 8–19% with marl recording the highest value Marl > CEMI > CEMII >Clinker >Iron ore> Raw meal>Limestone >Gypsum. SiO_2 content is an index for fineness or coerciveness and it determine the grindability of the cement clinker, level of water intake and strength of concrete [12]. Marl had the highest Al_2O_3 content, which will lead to high content of C_3A Table 2. Each of the oxides performs unique work during cement hydration; however, each content of the oxide must be in the right quantity during proportioning of raw materials [13]. The amounts of CaO according to European standard specification in ordinary Portland cement is in the range of 61-67 % [14] CEMI and CEMII cement are fell below the range. The European standard specified amount of SiO_2 in Portland cement should be within the range 19-23 % [14]. It was observed that all the tow types of cement are less than the specified limit Fig. 1. According to the European standard EN 197-1. The sum of the proportions of CaO and SiO_2 in cement should not be less than 50 % by mass. Similarly, the ratio by mass of CaO to SiO_2 should not be less than 2.0. CaO and SiO_2 in the analyzed cement samples exceeded 50 % by mass and have ratios above 2.0 [15]. The amounts of Al_2O_3 in the various types (Table 2) are within the range of 2-6 % specified by the European standard. The amount of Fe_2O_3 according to the European standard should be within the range, 0-6 %. The levels of Al_2O_3 and Fe_2O_3in all tow brands of cement used for this study are within their respective ranges specified by the European standard. Also, the contents of MgO were below the 5.0 % by mass recommended by the European standard. The levels of SO_3 in the cement brands were above the 1.5 %-2.5 % European standard recommended range in Portland cement Fig. 1.

The quality of Portland cement clinker depends on its chemical composition. Marl contains basically three oxides: SiO_2. Al_2O_3 and Fe_2O_3. Limestone decomposes to CaO and CO_2 during firing. SO_3 also appear in cement analysis, which comes from adding gypsum (4-6) % during clinker grinding. The percentage compositions of the various major and minor constituents of the cement samples are shown in Table 2.

The properties of the cement, such as its setting time and strength, are adjusted by the addition of gypsum and by grinding to specific degrees of fineness [16]. There are several brands of Portland cement available in the market but their chemical compositions are the same. Variations in physical properties occur due to the variation in the amount of chemical constituents [17]. The test Anova output indicated that each brand of Portland cement has variations no significant with respect to chemical composition. This is due to the differences that exist with individual factory proportioning of raw materials for Portland cement production. Quality of the cement is determined by composition ratio of the four compounds. Variations in chemical constituents affect the cement properties like, hardening/hydration, setting time, corrosion resistance, color, etc [18–19]. Qualitative and quantitative analyses are very important for a comprehensive characterization of cement and determination of phase composition of cement.

The heavy metals composition of Portland cement

The levels of 12 heavy metals *(*Arsenic, barium, lead, mercury, boron, strontium, Cadmium, Chromium, copper, manganese, nickel and zinc) in limestone, marl, iron ore, clinker, Gypsum, Cement CEMI, CEMII, and Kiln dust, were analyzed by Inductively Coupled Plasma Optical Emission Spectrometry ICP-OES-AS. Composition of the raw powder was prepared from raw materials limestone and marl, with the addition of iron ore. From the obtained results, it shows the next:

Total metal input to the limestone in order of decreasing ppm: Sr, Ba, Zn, Cr, V, Ni, Cu, Mn, Br, Pb, As and Cd **(**Fig .4).

Total metal input to the marl in order of decreasing ppm: Sr, Mn, Zn, Cr, Ba, V, Ni, Cu, Br, As, Pb and Cd (Fig .4). Limestone usually contains admixtures of clay substance or of iron compounds, which influence its color.

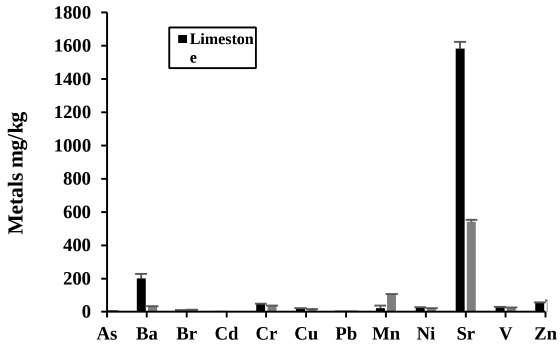

Fig. 4: Median contents of heavy metals in raw materials used for cement production.

Total metal input to iron ore (Fig. 5) in order of decreasing ppm Mn (1700ppm),Pb (2030ppm), Zn(2387), As(1813ppm), Ba(329 ppm), Sr(158ppm), Br(56ppm), Cr(22ppm), V(20ppm), Cu(14ppm), Cd(10 ppm), Ni(8 ppm) (Fig. 5).

Order of metal incorporation ppm (mg/kg) in clinker Sr, Mn, Ba, Zn, Cr, As, V, Pb, Ni, Br and Cu. Fig. 6.

Total metal input in gypsum in order of decreasing ppm Sr(2033ppm), Mn(136ppm), Ba(27 ppm), Br(5ppm), V(5ppm), Cr(4ppm), Cu(4ppm), Ni(4ppm), As (2ppm), Pb(1ppm) Fig. 7.

Total metal input in kiln dust in order of decreasing ppm Sr(1320 ppm), Ba (168.33), Mn (108) ppm)Zn (67ppm), Cr (49 ppm), As(43ppm), Pb(39ppm),V(38ppm), Ni(24), Br(14ppm), Cu (20ppm) and Cd(0.54ppm) Fig.8.

An important source of metal contamination from cement are the raw materials. This information is summarized in Tables 3 and 4.

In the case of Cr, the sources are limestone (44.87 ppm) marl (33.83ppm), and clinker (98 ppm). The chromium concentration was the highest in Portland cement CEMI (89 mg/kg) and the lowest in CEMII (82mg/kg) Fig. 9. The chromium is medium input by primary raw materials and represent an indelible non-volatile trace element of raw materials (clay, limestone and iron additives in particular) used in cement clinker production [20].

In the case of Ba sources are limestone (200 ppm) marl (34 ppm), and clinker (389 ppm). The Barium concentration was the highest in Portland cement CEMI (402mg/kg) and the lowest in CEMII (338 mg/kg).

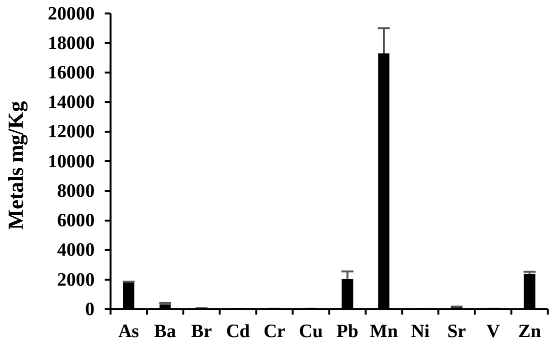

Fig. 5: Distribution of trace metal in iron ore (wt. %).

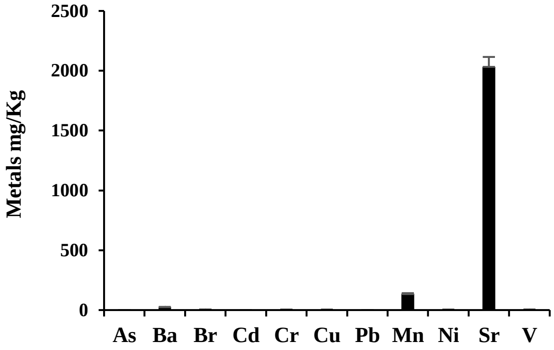

Fig. 7: Distribution of trace metal in gypsum (wt. %).

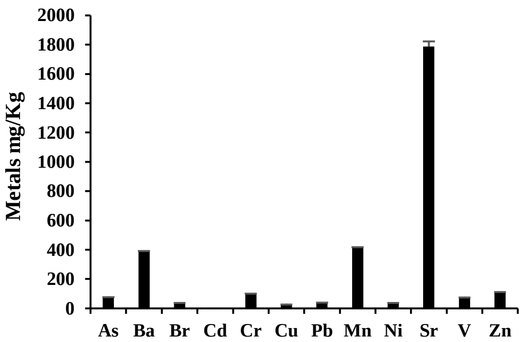

Fig. 6: Distribution of trace metal in clinker (wt. %).

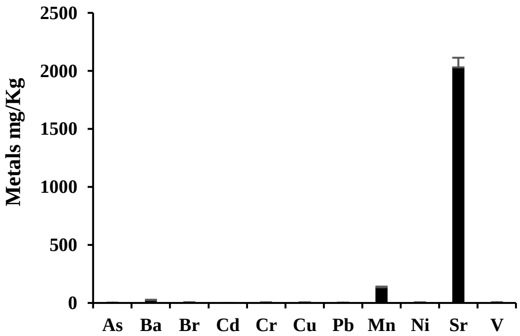

Fig. 8: Distribution of trace metal in kiln dust (wt. %).

In the case of boron, sources are limestone (8.37ppm Br), marl (10.20 ppm) and clinker (35.47 ppm). Boron concentration was the same in Portland Cement CEMI and CEMII (30mg/kg)

In the case of As, sources are limestone (2 ppm), marl (4 ppm), clinker (77ppm).The arsenic concentration was the highest in Portland cement CEMI (216 mg/kg) and the lowest CEMII (200.33). The arsenic High input by primary raw materials.

In the case of Pb, the sources are limestone (2.25 ppm), marl (2.43ppm) and clinker (38 ppm). The lead concentration was highest in Portland Cement CEMI (127mg/kg) and lowest in CEMII (124mg/kg). Lead is almost equally introduced by fuels and by secondary raw materials, such as iron ore, coal fly ash and ashes from burning process.

In the case of vanadium, sources are limestone (27 ppm) marl (24ppm) and clinker (73 ppm), the concentration was the highest in Portland Cement CEMI (141mg/kg) and the lowest in CEMII (137). Apart from raw materials, fuels are of importance. The typically utilised fuel oil coke is an important input material for vanadium. V, as is coal fly ash. Input by oil coke exceeds that of secondary fuels.

Ni sources are limestone (ppm 25) marl (22) and clinker (36 ppm). The nickel concentration was the same in Portland Cement CEMI and CEMII 46 mg/kg. Raw materials are a very important source of Nickel, significantly increasing the concentrations of chromium low-volatile trace elements Cr. The results show that concentration of heavy metals increases in the product of Portland cement this increasing come from refractory bricks lining the kiln, the grinding media

Strong increase of the concentration of Ba, Sr, Mn, Cr and Ni from raw material to clinker is clearly visible. It was determined that hardly volatile trace elements (Ba, Co,

Table 3: The percentage of metals in gypsum. limestone. clinker of cement CEMI (G= Gypsum L= Limestone C= Clinker Total =G+L+C).

Metals	G	L	C	Total
As %	0.025	0.06	73.39	73.474
Ba %	0.356	6.23	371.41	377.997
Br %	0.070	0.00	33.89	33.962
Cd %	0.000	0.01	0.00	0.014
Cr %	0.059	1.40	93.68	95.135
Cu %	0.058	0.67	24.08	24.813
Pb %	0.018	0.07	35.90	35.987
Mn %	1.813	0.66	395.94	398.415
Hg %	0.000	0.00	0.00	0.000
Ni %	0.062	0.77	34.27	35.101
Sr %	27.043	49.24	1707.34	1783.624
V %	0.071	0.85	70.08	70.995
Zn %	0.000	1.73	104.16	105.886
Total	29.576	61.69	2944.14	3035.402

Table 4. The percentage of heavy metals in gypsum, limestone clinker in cement CEMII (G= Gypsum L= Limestone C= Clinker Total =G+L+C).

	G	L	C	Total
As %	0.030	0.228	66.263	66.522
Ba %	0.436	24.220	335.341	359.99
Br %	0.085	0%	30.600	30.685
Cd %	0%	0.053	0%	0.0538
Cr %	0.071	5.424	84.583	90.079
Cu %	0.071	2.619	21.742	24.433
Pb %	0.0222	0.272	32.412	32.706
Mn %	2.222	2.583	357.486	362.292
Hg %	0%	0%	0%	0%
Ni %	0.076	2.974	30.945	33.995
Sr %	33.143	191.425	1541.536	1766.104
V %	0.087	3.292	63.272	66.651
Zn %	0%	6.709	94.045	100.755
Total	36.246	239.574	2658.229	2 934.279

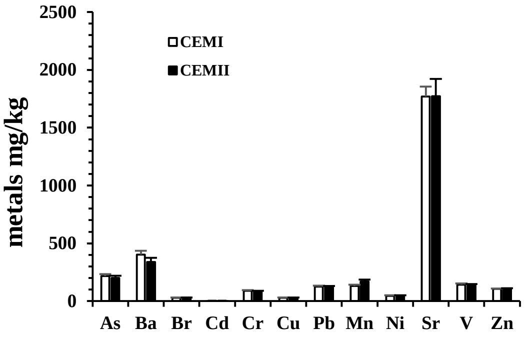

Fig. 9: Distribution of trace metal in Portland cement CEMI (wt. %) and CEMII (wt. %).

Cr, Cu, Ni, Zn and V) are mainly incorporated in the main hydraulic clinker phases C_3S, C_2S, and C_4AF [21]. According to the above analysis (Fig. 8), it was confirmed that all the refractory metals (Ba, Sr, Mn, Ni and V) are mostly retained by cement kiln process solids. The concentration of toxic heavy metals in the cement samples are shown in Fig. 9.

The metal with highest input rate is Sr, closely followed by Mn and Ba. Interestingly, the portland cement CEMI contained higher concentrations of arsenic, lead, barium, Vanadium and chromium than CEMII. Metal compounds are introduced into the furnace with a raw materials and iron ore , but the most of them originate from the raw materials. Iron ore is a correction material, iron ore was assigned to the group of secondary raw materials. Raw materials or interground additives were used, if iron ore was used in the raw powder, the average chromium and copper concentrations would have been increased significantly in cement. The overall metal material balance could be performed by monitoring the mass metal rates for all inputs and outputs of the cement kiln**.** Due to the conservation of metals in the combustion process, theoretically, the percentage of mass closure should be in the vicinity of 100 % [22]. Thus it can be concluded for any metal added to the cement kiln with raw materials or fuels, the most of them will be retained by cement kiln process solids, while the less of them will appear in the stack gas stream. *Cipurkovic*, 2014 [23] has concluded for any metal added to the cement kiln with raw materials or waste derive fuels, less than 1 % of the input will appear in the stack gas stream, while 99 % of the input will be retained by cement kiln process solids. *Brandt*, 1995 [24] reported that typical cement raw materials contain 25 mg/kg of Cr, 21 mg/kg of Cu, 20 mg/kg of Pb and 53 mg/kg of Zn and about 50% of the total Cd, Cu and Zn load in cement are introduced through raw materials.

Portland cement CEMI is produced by mixing clinker (95,56 %), limestone (3.11 %) and gypsum (1.33 %). Portland cement CEMII is produced by mixing clinker (86.28 %), Limestone(12.09 %) and gypsum (1.63%) Table 5. Clinker and Portland cement exhibit slight element concentration differences only, as Portland cement consists mostly of clinker.In clinker (Fig .8) there are high concentrations of trace elements Ba (388), Br (35), Cr (98), Mn (414), Ni (36mg/kg), Sr (1787ppm) and Zn (109 ppm). It was determined that hardly volatile trace elements (Ba, Co, Cr, Cu, Ni, Zn and V) are mainly incorporated in the main hydraulic clinker phases C_3S, C_2S, and C_4AF [25].

Kiln dust from the cement factory in north Tunisia contains trace elements, such as As, Ba, Cr, Pb, Cu, Mn, Ni, Sr and Zn (Fig. 9). About 17 trace elements namely, antimony, arsenic, lead, cadmium, chromium, cobalt, copper, manganese, nickel, thallium, tin, vanadium, zinc, beryllium, selenium, tellurium and mercury have been reported in cement kiln dust [26]. In cement, the metal with highest input rate is Sr, closely followed by Ba and Mn. Analysis showed that metal compounds are originate from the raw materials. For the most elements studied, the raw material feed is the principal source of metal compounds in the total feed to the kiln. The increase in metal concentration (Ba, Sr, Mn, Cr, Ni) from raw meal to clinker results from CO2 discharge and the associated mass loss. Zn and V content. Come from the fuel used tires, heavy fuel oil, etc [27]. This increase is assumed to be caused largely by fuels Approximately 75-90% of metal strontium, manganese, chromium, nickel, vanadium, copper, were added with raw material feed; Sr is mostly from limestone; Input of more than 50% of Ni, V and Cu originate from ash [25] chromium is mostly input from limestone. All (non volatile) metals generally tend to be incorporated into the clinker, while the lower part, especially volatile and semi-volatile metals accumulates in the cement dust. Cement dust contains heavy metals like metals like nickel,cobalt , lead, chromium, pollutants hazardous to the biotic environment with impact for vegetation, human andanimal health [28]. The mean trace

Table 5: The percentage of gypsum, limestone and clinker in CEMI and CEMII.

	CEM I	CEMII
Gypsum %	1.33	1.63
Limestone %	3.11	12.09
Clinker %	95.56	86.28

element concentration in cement is caused by the input of secondary fuels and inter ground additives. Raw meal (limestone, marl and iron ore) was combined with a fuel mix causing the highest trace element concentrations in Portland cement. According to the previous studies, the presence of heavy metals (especially chromium) in cement kiln is obvious [29]. Refractory in cement kiln can adsorb quantities of heavy metals exist in the kiln. Use of this refractory could contribute to a surge in chromium levels to the clinker during the first use of kiln after re-bricking.

CONCLUSIONS

Our study is the first for determination of various heavy metals in raw materials, such as gypsum, cement and kiln dust. Portland cements CEMI and CEMII in cement factory in North Tunisia. The measurements of the heavy metal content in Portland cement showed interesting results. Theoretical X-ray diffractograms are very important for establishing the identity of each component of cement and its crystal phase and its relative abundance in cement. The quality of Portland cement clinker in north Tunisia depends on its chemical composition. Marl contains three oxides: SiO_2, AI_2O_3 and Fe_2O_3. Limestone decomposes to CaO and CO_2 during firing. SO_3 also appear in cement analysis, which comes from adding gypsum (4-6) % during clinker gridding. Namely, CEMII contained lower concentrations of Ba, Mn and As than CEMI. CEMII had the least amount of all trace metals of the materials tested. It is possible that the raw material for CEMI and CEMII is similar but different from the raw materials for CEMII. The concentrations of the 10 heavy metals (Ar, Br, Pb, Hg, Ba, Sr, Cd, Cr, Cu, Mn, Ni and, Zn,) in CEMI showed no significant difference $p<0.05$ with those in CEMII. In a comparison of CEMII, had less or statistically equal contents of seven heavy metals (Boron, cadmium, copper, nickel, manganese, and strontium) compared with CEMI. These differences in heavy metal contents could be considered before use of Portland cement. The distribution of elements in different streams in the process of sintering indicates that most of the trace elements incorporated in the mineral phases of clinker. Due to different factors in cement production such as raw materials, refractory bricks lining the kiln, wear metal from raw mill grinding process, fuels and additives many of heavy metals have the chance to enter the clinker and final cement product. For the most elements studied, the raw material is the principal source of metal compounds in the total metals in cement. Due to the incorporation of heavy, toxic metals in the clinker minerals, they are entered in the cement and concrete later in which to linger for many years. Cement is important from the economic point of view but it could contain heavy elements posing threat to the environment and human health. Furthermore, future investigation are needed to underline the toxic effects of the founded elements.

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REFERENCES

[1] Environmental Road Mapping Initiative, Iron and Steel: Impact, Risks and Regulations summary, "Ann Arbor, MI: National Center Manufacturing Sciences (2004).

[2] Goguel R.L., St John D.A., Chemical Identification of Portland Cements in New Zealand Concretes, *Cement and Concrete Research*, **23**(1): 59-68 (1993).

[3] Dammaschke T., Gerth H.U., Züchner H., Schäfer E., Chemical and Physical Surface and Bulk Material Characterization of White ProRoot MTA and Two Portland Cements, *Dental Materials*, **21**(8): 731-738 (2005).

[4] Ahmed U.J., Birnin–Yauri U.A., Dangoggo S.M., Studies on Leachability of Chromium from Ordinary Portland Cement, *Biological and Environmental Sciences Journal for the Tropics*, **6**(2):89-91 (2009).

[5] Bucchi, Influence of the Nature and Preparation of Raw Materials on the Reactivity of Raw, Mix", *7th, International Congress of Chemistry*, Paris, **1**:3-43 (1980).

[6] Taylor H.F.W., "Cement Chemistry", Academic Press, London.;10-69 (1990).

[7] Falah F.B.H. Chemical Analysis of Ordinary Portland Cement of Jordan, *Assiut University Bulletin for Environmental Researches*, **14**(1):1-9 (2011).

[8] Kong Q., Chen L., Wang L., Preparation of Sub-Standard Samples and XRF, Analytical Method of Powder Non-Metallic Minerals, *Guang Pu Xue Yu Guang Pu Fen Xi*, **32**(5):1405-1409 (2012).

[9] Bediako1M., Amankwa E.P., "Analysis of Chemical Composition of Portland cement in Ghana": A Key to Understand the Behavior of Cement. *Hindawi Publishing Corporation Advances in Materials Science and Engineering*, Volume, Article ID 349401, 5 Pages (2015).
http://dx.doi.org/10.1155/2015/349401

[10] Punmatharith T., Rachakornkij M., A. Imyim A., Wecharatana M., Co-Processing of Grinding Sludge as Alternative Raw Material in Portland Cement Clinker Production, *Journal of Applied Sciences*, **10**(15):1525-1535 (2010).

[11] Lam H.K., Barford J.P., McKay G., Utilization of Incineration Waste Ash Residues as Portland Cement Clinker, *Chemical Engineering Transactions*, **21**: 757-762(2010).

[12] Frias M.I., Sanchez R., Determination and Quantification of Total Chromium and Water Soluble Chromium Content in Commercial Cement, *Cement and Concrete Research*, **25**(2): 432-43 (1995).

[13] Huntzinger D.N., Eatmon T.D., A Life-Cycle Assessment of Portland Cement Manufacturing: Comparing the Traditional Process with Alternative Technologies, *Journal of Cleaner Production*, **17**(7): 668-675 (2009).

[14] Tamas K.S., "Study Aid 1.2- Construction/Building Materials I for Bsc (Civil and Architect Engineering). Ybl Miklós College of Technology", Département des Matériaux de Construction et du Contrôle de la Qualité, Hongrie; (2010).

[15] (ESEN) European Standard EN 197-1, Cement - Part 1: Composition. Specifications and Conformity Criteria for Common Cements Prepared by Technical Committee CEN/TC 51 (2000).

[16]Wagner K., Vassilopoulos M., The European Cement Industry-Background Assessment for the IPTS BAT-Competitiveness Project (2000).

[17] Falah F.B.H., Chemical Analysis of Ordinary Portland Cement of Jordan, *Assiut University Bulletin for Environnemental*, **14**(1):1-9 (2011).

[18] Pandey G., Shukla S., "A Text Book of Chemical Technology", Vol. 1, Vikas Publishing House, New Delhi, (1980).

[19] Vogel A., Text Book of Quantitative Inorganic Analysis, The English Language Book Society and Longmans, Green & Co.Ltd, 5th edition, (1989).

[20] Eštoková A., Palaščákováa L., Singovszkáb E., Holubb E., Analysis of the Chromium Concentrations in Cement Materials, *Procedia Engineering*, **42**: 123–130 (2012).

[21] Schmidt R., "Introduction to Clinker and Cement Phase Analysis", Workshop, Karlsruhe, Germany (2004).

[22] Tervahatty H., Lodenius M., Tulisalo E., Effects of the Reduction of Cement Plant Pollution on the Foliar and Bark Chemical Composition of Scots Pin, *Boreal Environment Research*, **6**: 251-259 (2001).

[23]Cipurkovic A., Trumic I., Hodžic Z., SelimbašicV., Djozic A., Distribution of Heavy Metals in Portland Cement Production Process Pelagia Research Library, *Advances in Applied Science Research*, **5**(6): 252-259 (2014).

[24] Brandt A.M., Cement-Based Composites: Materials, Mechanical and Performance, 1st ed., E& FN Spon, London (1995).

[25] Achternbosch M., Bräutigam K.R., Gleis M., Hartlieb N., Kupsch C., Richers U., Stemmermann P., Heavy Metals in Cement and Concrete Resulting from the Co-Incineration of Wastes in Cement Kilns with Regard to the Legitimacy of Waste Utilisation Karlsruhe: Forschungs Zentrum Karlsruhe (2003).

[26] Tervahattu H., Lodenius M., Tulisalo E., Effects of the Reduction of Cement Plant Pollution on the Foliar and Bark Chemical Composition of Scots Pine, *Boreal Environment Research*, (6): 251-259 (2001).

[27] Tamás F.D., Abonyi J., Puertas F., Trace Elements Based Classification on Clinkers. *Application to Spanish Clinkers. Materiales de Construcción*, **263-264** (51): 85-96 (2001).

[28] Kumar S.S., Singh D., Baby S., Singh N.A., Vivek K., Impact of Dust Emission on Plant Vegetation of Vicinity of Cement Plant, *Environmental Engineering and Mangement Journal*, **7**(1): 31-35 (2008).

[29] Linda Hills, Vagn C., "Johansen Hexavalent Chromium in Cement Manufacturing:Literature Review", PCA R&D Serial No. 2983, Portland Cement Association 2007 Chen W.-K., Linear Networks and Systems (Book Style), Belmont, CA:Wadsworth. 123-135 (1993).