

Distribution of heavy metals in Portland cement production process

¹Amira Cipurkovic, ¹Ilvana Trumic, ¹Zorica Hodžić, ²Vahida Selimbašić and ²Abdel Djozic

¹Department of Chemistry, Faculty of Natural Science, University of Tuzla, Tuzla, Bosnia and Herzegovina

²Department of Environmental Protection, Faculty of Technology, University of Tuzla, Tuzla, Bosnia and Herzegovina

ABSTRACT

The potential negative impact of heavy metals on the ecosystem and human health in particular is evident. People are exposed to heavy metals through plant and animal food, water, soil and air. In industrial regions environment is usually contaminated with heavy metals. The theme of this research is to determine which metal elements are introduced into the production process of Portland cement in a cement factory in Lukavac (FCL) and to determine the metal input rate and their distribution at the entrance and exit of the process. In the process of production of cement clinker in FCL, metal elements are mostly entered by primary raw materials: limestone, marl lime, clay stone, sand; coal fly ash as secondary raw material and brown coal as regular fuel, generally come out with a finished solid products: clinker, cement and cement dust from the bag filter or gases. Coal fly ash and natural gypsum are used as additives for PC production. All refractory metals generally tend to be incorporated into the clinker, while the lower part, especially volatile and semi volatile metals (Cd, Hg), accumulates in the cement kiln dust. Most metals in cement are infused with clinker, except mercury and cobalt, which are entered from the ashes. Concentrations of metals at the entrance and exit of the kiln were determined using a Perkin - Elmer Inductively Coupled Plasma-Optical Emission Spectrometer.

Keywords: heavy metal, Portland cement, clinker, cement kiln dust, environment

INTRODUCTION

Cement is an important world-wide produced binding agent for construction industry. A central process step during the manufacturing of cement is the production of intermediate product clinker. For this production, inorganic raw materials are burnt at temperatures in the range of 1500 °C. Cement clinker, contained of synthetic minerals, is grained in fine powder, together with determined quantity of gypsum, producing hydraulic binder - cement. Basic raw-materials for cement production are mineralogical materials of carbonate character (limestone component) and raw-materials of acid character (clay component).

In Bosnia and Herzegovina, Portland cement (PC) is produced in Cement Factory of Lukavac (FCL), the member of *Ein Unternehmen der Asamer Gruppe* from Austria, applying domestic primary or secondary raw-materials. Mixing of marl-clay (as primary) or coal fly ash from TPS Tuzla (as secondary raw material), with limestone and quartz sand, raw-mixtures were obtained. From prepared raw-mixtures, cement clinker was produced in rotary-kiln by dry process. In the kiln-process, hard and brown coals were used as regular fuels (50 % of imported and 50 % of domestic coal). It means that in this process, use of waste is not an energy carrier in the burning process of clinker production, but waste is used as an alternative inorganic raw material (electro-filter coal ash).

Different raw materials, primary or secondary substitute of inorganic raw material, as fuels, may contain varying trace element concentrations. Their use leads to the question of where the trace elements of these materials remain. The presently used procedures for cement manufacture cause the trace elements to be either transferred into the product cement or emitted with the exhaust gas into the environment. The question to which extent trace elements are transferred into the cement and potential environmental impacts becomes increasingly important. In analysis, the

term of trace elements generally refers to elements of less than 100 ppm concentration. This term is kept for these elements to distinguish them from the main elements that reach concentrations in the percent range.

In cement manufacture, it must be guaranteed that the use of waste is proper and not harmful. This paper researched the distribution of input and output metal elements when a primary input material, marl clay was substituted by appropriate proportion of fly ash as secondary raw material during cement clinker production in FCL. The discussion of effects of its use on plant operation, and product quality of the cement clinker was reported earlier [1].

Production of cement

Cement production starts with the extraction of the raw materials and their subsequent pre-crushing in the quarry located in the vicinity of cement works. With the ratio of raw materials being specified exactly, a mixture is produced, if necessary, by adding correction materials, such as sand, iron ore and clay. Apart from natural raw materials, waste materials containing lime, aluminate, silicate, and iron are used as raw materials substitute.

This mixture of raw materials is milled to raw meal and, at the same time, dried with the residual heat of the kiln of gases. In the downstream electrostatic precipitator, the raw meal is separated and subsequently transported to the raw meal silos. Via the pre-heater, the dust-like raw meal is fed into the rotary kiln. By means of the burning process at 1250 to 1599 °C, clinker granules are formed. The energy required is supplied by the combustion of coal in a burner at the end of the rotary kiln (primary combustion) and partly also at the beginning of the rotary kiln (secondary combustion). The hot flue gases generated by combustion, flow through the rotary kiln and pre-heater in opposite direction to the solids. The clinker leaving the rotary kiln has to be cooled down. [2, 3]

Clinker represents the most important constituent of the Portland cement produced by the addition of gypsum or other inter-ground additives (limestone, coal fly ash etc.) and subsequent crushing. The dust-containing off-gas from the kiln is cooled down in the off-gas cooler subjected to subsequent de-dusting in the bag filter. The separated dust, and the trace elements contained in it are partly returned to the cement production process during cement milling and partly added to the raw meal again. These operations considerably influence the temperatures and material flows between the meal, kiln system, and bag filter of the plant. Part of the filter dust is removed and, hence, does not enter the raw meal. Thus, the trace element cycle is relieved. The discharged material, however, usually enters the cement as an inter-ground additive [4, 5].

Aim and strategy of the investigation

The aim of this project was to demonstrate the effect of input materials, inter-ground additives and fuel on metal element concentrations of cement. Coal fly ash was applied as both, inter-ground additive and raw material. Estimation of the trace element contents of reactants and products of cement kiln is based on a data of trace element concentrations determined in all different materials used, using average values.

It is well-known that the metal compounds present in solid and fuels are not destroyed by the combustion process in the kiln. The cement kiln will redistribute any metals in the input materials by releasing them in stack gas emissions, cement kiln dust or in the cement product, clinker. Although a metal compound is changed during the combustion process, a metal is not destroyed. Therefore, any metal present in the fossil fuel or raw feed, natural or waste, will be present either in the kiln stack emissions, the cement kiln dust (CKD) or the clinker. The metals entering a cement kiln via fuel or raw material feed may be categorised as volatile, semi-volatile and refractory, based on their volatiles [5, 6]. It may be assumed that a higher trace element concentration in an input material inevitably causes an increase in the trace element concentrations of cement.

Based on trace element concentrations of input materials, raw meal, clinker and cement determined, for further investigation 10 elements were selected: barium, strontium, cadmium, chromium, cobalt, copper, manganese, nickel, vanadium and mercury. Some of these metals, Cd, Cr, Ni and Hg, are known as toxic or suspected to be carcinogens. The air emissions of metals are of greatest concern due to the health risks resulting from this release [7]. Several studies in cement kilns have attempted to study the fate and distribution of metals found in the waste fuels [8, 9]. The amount of mercury transferred into clinker or cement can hardly be determined due to its high volatility.

Co-incineration of waste in the production of cement is governed by directives, standards, regulations etc. In Bosnia and Herzegovina, the handling of wastes and their incineration are subject of the Regulation on conditions for the operation of waste incineration plants [10].

MATERIALS AND METHODS

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 the whole production process from raw-materials to products and its chemical and physical properties were collected. Samples of fuel, raw-materials and products were taken from FCL in August 2012.

Determination of Heavy Metals Concentration

Triplicate subsamples of approximately 1 g of well homogenized solid samples were accurately weighed on an analytical balance and then burnt on filter papers and glowd in platinum dishes at temperature of 1000° C to remove organic matters. After that, samples were transferred into glass digestion tubes and digested in concentrated chloric acid and diluted to a final volume of 500 cm³ using double distilled water. The filtrate was examined for the input and output concentrations of metals: Ba, Sr, Mn, Ni, Cu, Cr, Co, Cd and V by *Inductively Coupled Plasma-Optical Emission Spectrometer*, ICP-OES OPTIMA 2100 DV, Perkin-Elmer, with the standard of 100 mg/dm³ for metals [11, 12]. The results were expressed in mg/dm³ of filtrate. Data presented are average of three replications. Sampling and analysis were made following European standards for cement EN 197-1: 2005, EN-197-2: 2004, EN-196-1:1994. [13].

RESULTS AND DISCUSSION

Metal Distribution in Input Streams

2800 tons of raw-meal is daily prepared for clinker production in FCL. Composition of the raw-meal was prepared from raw-materials in the next ratio: limestone : fly ash : sand = 80,5 : 13,3 : 6,2 (wt. %), with addition of 250 t/day of coal as fuel. Regarding the composition of the raw meals, various cement standards (lime standard, silicate module, alumina standard) were considered. It must be taken into account that the amounts of input materials used does not include any data on precipitator ash (CKD) and bypass dusts in the process.

In this section the total metal input rate to the kiln (kg/h) and the distribution of metals in the input stream (mass fraction, wt. %) during the burning process were determined. The results are shown in figure 1 and figure 2.

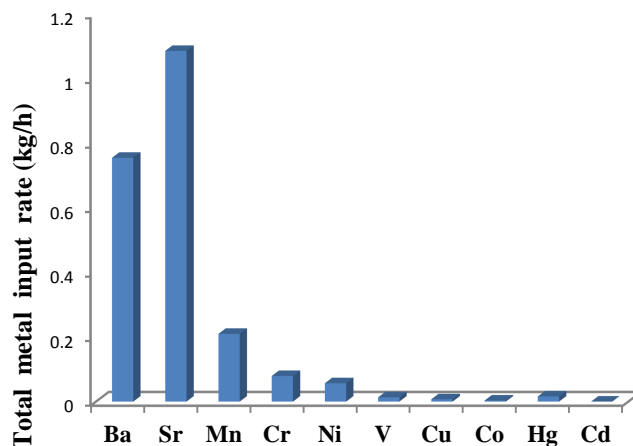


Figure 1. Total metal input rate (kg/h)

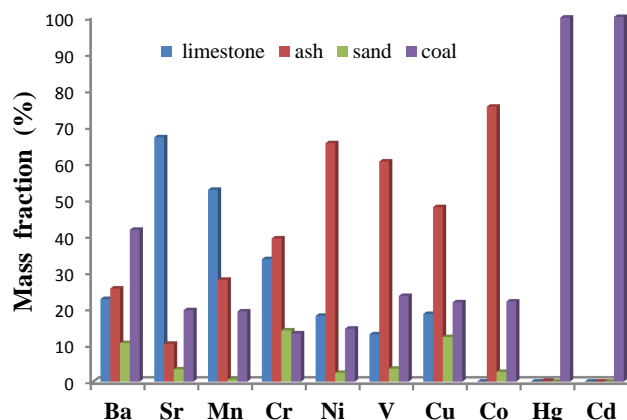


Figure 2. Distribution of trace metal input (wt. %)

From the obtained results, it shows the next:

Order of total metal input to the kiln (kg/h):

Sr > Ba > Mn > Cr > Ni > Hg > V > Cu > Co > Cd.

Order of distribution of individual trace elements to raw-meal (wt.%) from various input pathways:

Ba: coal >> ash > limestone > sand
 Sr: limestone >> coal > ash > sand
 Mn: limestone >> ash > coal > sand
 Cr: ash >> limestone > sand ≈ coal
 Ni: ash >> limestone > coal > sand
 V: ash >> coal > limestone > sand
 Cu: ash >> coal > limestone > sand
 Co: ash >> coal > sand
 Hg: coal >> ash
 Cd: coal

Order of input trace elements (wt.%) from various raw-materials:

from coal: Cd > Hg > Ba > V > Co > Cu > Sr > Mn > Ni > Cr
 from limestone: Sr > Mn > Cr > Ba > Cu > Ni > V
 from ash: Co > Ni > V > Cu > Cr > Ba > Mn > Sr > Hg
 from sand: Cr > Cu > Ba > V > Sr > Co > Ni > Mn

Summary, order of input metals from raw-meal (wt.%):

Cr > Ni > Mn > Sr > Cu ≈ Co > V > Ba > Hg

As shown, the metal with highest input rate is Sr, closely followed by Ba. Analysis showed that metal compounds are introduced into the furnace with a raw materials and coal as fuel, but the most of them originate from the raw materials. Mass fraction of metals originating from coal is much smaller for all metals, except for barium (about 40% input of Ba is from coal). According to figure 2, the metal compounds which may be completely attributed to coal include Cd and Hg (99,8 %).

Metal distribution in the solid products: clinker, clinker dust and cement

At daily production of clinker in FCL of 1800 t, about 5 % wt. (90 t/day) is being separated as cement kiln dust (CKD) which is collected in bag-filters and mixed with raw-materials for burning process in rotary kiln. In this section the metal output rate and the distribution of metals in the solid products, clinker and CKD during the burning process were determined. The results are shown in figure 3 and figure 4.

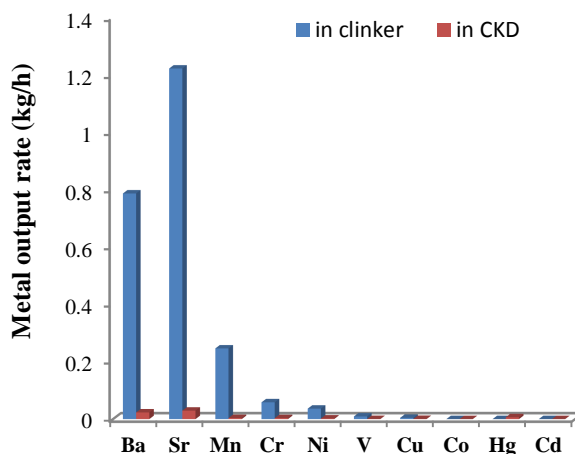


Figure 3. Metal output rate (kg/h) in solid products

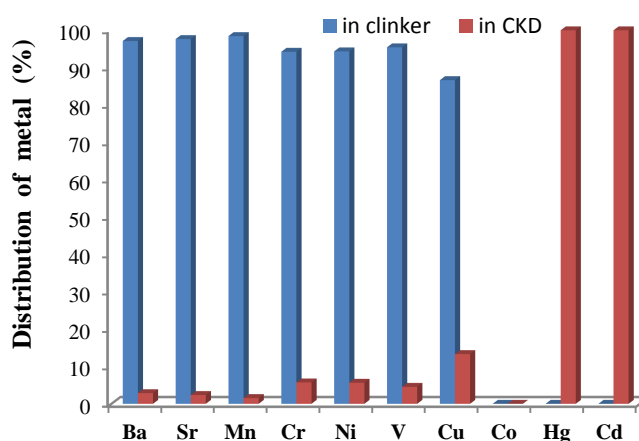


Figure 4. Distribution of metal output, clinker and CKD (wt. %)

Order of metal incorporation (kg/h) in clinker: Sr > Ba >> Mn > Cr > Ni > V > Cu > Cd.

The tendency of some trace elements to accumulate in the CKD can be summarized in the following order (wt. %): Hg = Cd > Cu >> Cr > Ni > V > Ba > Sr > Mn.

Strong increase of the concentration of Ba, Sr, Mn, Cr and Ni from raw meal to clinker is clearly visible. It exceeds the increase in concentration resulting from CO₂ discharge and the associated mass loss (for 1 t of clinker 1,55 t of raw meal are needed). According to the above analysis, it was confirmed that all the refractory metals (Ba, Sr, Mn, Ni, V) are mostly retained by cement kiln process solids. These data indicate that all refractory metals generally tend to be incorporated into the clinker, while the volatile and semi-volatile metals accumulate in CKD.

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 %. One of the most useful measures of determining the potential for release of metal compounds by a cement kiln when burning wastes is to give the percent of the input metal that is emitted with stack gas. However, the accurate monitoring of input and output streams is complicated due to factors such as low concentrations of trace elements with values close to or below detection limits, inability to maintain constant input and output flows throughout the test burn and the inability to capture volatile species such as mercury in the sampling system. Furthermore, the measurements were made more difficult since the test burns were conducted as full scale in actual cement kiln.

Emission of trace metals and the other gas products from rotary kiln were measured by specialized Department of environmental protection, heating and air conditioning company OČOT from Trenčín (Czech Republic) in

accordance with paragraph 5 of Article 10 of the Directive 2000/76/ES of the European Parliament and of the Council [14]. It was determined emission of Cr, Co, Cu, Mn, Ni, Cd and V less than $1,55 \text{ mg/m}^3$, while emission of Hg in the air was $0,47 \text{ mg/m}^3$.

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.

Early measurements showed that the percent of input emitted for all refractory metals the (Ba, Cr, V, Ni) is below 0,1 % confirming that more than 99,9 % of these metals are retained by the cement kiln process solids. The percent of input emitted for volatile and semi-volatile metals (Cd, Hg) is below 0,75 % confirming that more than 99,25 % of these metals are retained by the cement kiln process solids. It was 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 [5].

Daily production of Portland cement in FCL is about 2300 t. It is produced mixing of clinker (78 %), fly-ash (17 %) and gypsum (5 %). The total metal input rate to the PC and its distribution within input streams are shown in figure 5 and figure 6.

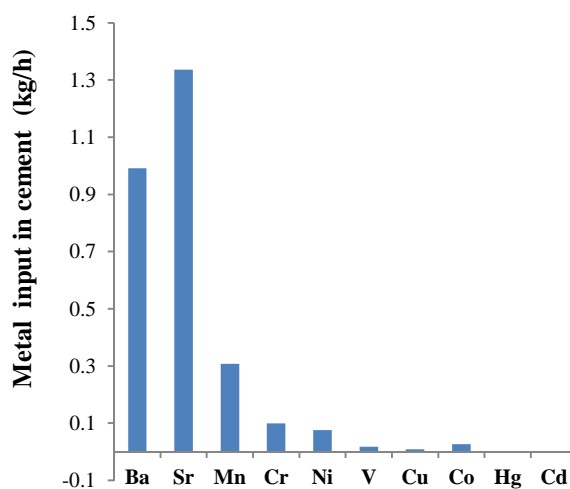


Figure 5. Total metal input in cement

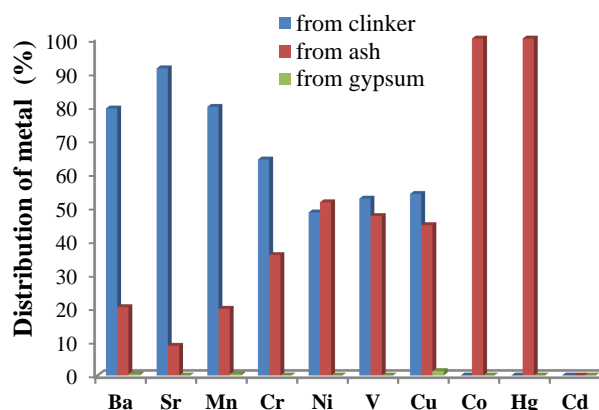


Figure 6. Distribution of metals in cement

Order of total metal input rate to the cement (kg/h): Sr > Ba > Mn > Cr > Ni > Co > V > Cu > Hg

Order of distribution of individual trace elements to PC (wt. %) from various input pathways:

Ba, Mn: clinker >> ash > gypsum

Cr, Cu: clinker > ash >> gypsum

Sr: clinker >> ash

V: clinker > ash

Ni: ash > clinker

Co, Hg: ash

Order of input trace elements (wt. %) from various materials into cement:

from clinker: Sr > Mn > Ba > Cr > Cu > V > Ni
 from gypsum: Cu > Mn > Ba > Cr
 from ash: Co > Hg > Ni > V > Cu > Cr > Ba > Mn > Sr

Clinker and Portland cement exhibit slight element concentration differences only, as PC consists mostly of clinker. By using the bottom-up approach, it was demonstrated clearly that the use of waste, coal fly ash as secondary raw material and additive, leads to an increased concentration of Ba, Sr, Mn, Cr, Ni, V, Cu and Co concentration in cement.

The data of binding of trace elements and their concentration in different phases of cement minerals ($C_3S = 3CaO \cdot SiO_2$, $C_2S = 2CaO \cdot SiO_2$, $C_3A = 3CaO \cdot Al_2O_3$ and $C_4AF = 4CaO \cdot Al_2O_3 \cdot Fe_2O_3$) are very rare. In order to determine the distribution of trace elements in various phases of cement some literature sources were used [5, 6]. Trace element contents (ppm) in ordinary Portland cement (OPC), PC clinker, electrostatic precipitator ash (EPA) and CKD were analysed from different sources in which comparison is hardly possible because they depend strongly on the operating parameters in different parts of cement plant and from the composition of the raw materials, which vary strongly. The trace element content of individual clinker phases is important. Since the particular trace element contents in technical clinkers are too low for direct analytical proof, only data on maximum solubility of some trace elements in the main clinker phases are available from laboratory experiments (Table 1).

Laboratory researches showed that the trace elements, mercury, arsenic, tin, cadmium, lead and thallium accumulated in filter dust and little or nothing incorporated in the main phases of clinker, while barium, chromium, copper, nickel, molybdenum, antimony, zinc, tellurium, beryllium, cobalt and vanadium were incorporated into the clinker phases. Maximum incorporation of trace elements in the clinker phases was determined in laboratory experiments at high concentrations of trace elements. 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 [15, 16]. Concentration of these elements was not increased in the fly ash. In addition, a trace element can be adsorbed to the surface of the crystalline minerals of clinker. However, it is correlated with an increase in volatility.

Table 1. Trace element contents (wt. %) in PC clinker minerals [5]

element	C_3S	C_2S	C_3A	C_4AF
Ba	2	0,27		
Cd	0,6	0,26		0,14
Co	0,4	0,25	0,5	4
Cr	1,2	3,25		
	0,57	1,11	0,1	0,5
	0,73	0,42		
Cu	0,7	0,2	0,4	1,1
Ni	0,5	0,25	0,3	3
V	0,5	1,3	0,1	0,2
	0,34	0,17		

CONCLUSION

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 CO_2 discharge and the associated mass loss. Approximately 75-90% of metals strontium, manganese, chromium, nickel, vanadium, copper, cobalt were added with raw material feed; Sr and Mn are mostly from limestone; Cr, Ni, V, Cu and Co from fly-ash. Input of more than 50% of Ni, V and Co and about 50% of Cu originate from ash. About 75% input of Cr is from limestone and ash. All (non volatile) metals generally tend to be incorporated into the clinker, while the lower part, especially volatile and semi-volatile metals (Cd, Hg), accumulates in the cement dust. Volatile and semi-volatile metals, as well as fine particles of cement dust, possibly, depending on the efficiency of the existing filters in the factory, can broadcast the gaseous products. These properties can have a significant impact on the distribution of metals at high temperatures in the sintering process. Metals enter the cement from clinker, ash and gypsum. Most metals are infused with clinker, except mercury and cobalt, which are entered from the ashes. 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 (C_3S , C_2S , C_3A , and C_4AF). 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. Thus preventing or reducing their negative impact on the environment.

Acknowledgment

The authors thank to the management of Cement Factory in Lukavac (FCL) and Federal Ministry of Education and Science of Bosnia and Herzegovina, (FMON, as a part of the project under position “Transfer for science of importance for Federation”) for financial support of this research.

REFERENCES

- [1] Cipurković A, Hodžić Z, Selimbašić V, Crnkić A, Dedić A, Trumić I, The influence of Fly ash and Marl-clay from Tuzla Canton as Raw-materials on PC Clinker Production, 8th International Soil Science Congress “Land Degradation and Challenges in Soil Management”, Izmir/Turkey, 15-17 May **2012**. Proceedings Book, III, 258.
- [2] Brandt AM, *Cement-Based Composites: Materials, Mechanical and Performance*, 1st edition, E& FN Spon, London, **1995**.
- [3] Barnes P, *Structure and Performance of Cements*, Applied Science Publishers, London and New York, **1983**.
- [4] Ishikawa Y, Herat S, *Green Energy And Technology*, in: *Waste of Energy*, Springer LinkVerlag, **2012**, 137.
- [5] Achternbosch M, Bräutigam K, 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, Germany, **2003**.
- [6] Herat S, *Environment Protection Engineering*, **1997**, 23, 25.
- [7] Gierzatowich R, *Environmental Science Research*, **2000**, 58, 55.
- [8] Kaantee U, Zevenhoven R, Backman R, Hupa M, *Modelling a Cement Manufacturing Process To Study Possible Impacts of Alternative Fuels, Extraction and Processing*, Division Meeting on Recycling and Waste Treatment in Mineral and Metal Processing: Technical and Economic Aspects, Lulea, Sweden, **2002**.
- [9] Johannesson M, *A Review of Risks Associated to Arsenic, Cadmium, Lead, Mercury and Zinc*, The Market Implications of Integrated Management of Heavy Metals Flows for Bioenergy use in the European Union, Kalmar University, Sweden, **2002**.
- [10] „Official Gazzete of Bosnia and Herzegovina“, No 12/05.
- [11] Skoog DA, Holler FJ, Nieman TA, *Principles of Instrumental Analysis*, Saunders College Publishing, **1998**.
- [12] Jenkins R, *X-ray Techniques: Overview*, *Encyclopedia of Analytical Chemistry*, John Wiley & Sons, Ltd, Chichester, **2000**.
- [13] European Standard for common cements, EN 197-1: 2002. Cement – Part 1: Composition, specifications and conformity criteria for common cements.
- [14] Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000. on the incineration of waste.
- [15] Schmidt R, *Introduction to Clinker and Cement Phase Analysis*, Workshop, Karlsruhe, Germany, **2004**.
- [16] Tervahattu H, Lodenius M, Tulisalo E., *Boreal Environment Research* **2001**, 6, 251.