Glasnik hemičara i tehnologa Bosne i Hercegovine

Bulletin of the Chemists and Technologists of Bosnia and Herzegovina

2018

51

47-52

Print ISSN: 0367-4444

Online ISSN: 2232-7266

UDC: 66.0-033.24(497.6)

Technical Paper

Characterization of raw materials and final product in the cement production

Đukić, D.[a*], Lazić, D.[b], Drljača, D.[c], Imamović, M.[d]

[a]*V-Z Zaštita d.o.o. Occupational Safety Company, Put srpskih branilaca 15H,Banja Luka, Bosnia and Herzegovina*

[b]*Faculty of Technology Zvornik, University of East Sarajevo,Karakaj 34 A,Zvornik, Bosnia and Herzegovina*

[c] *Faculty of Technology, University of Banja Luka, Vojvode Stepe Stepanovića 73, Banja Luka, Bosnia and Herzegovina*

[d] *Holding Company Cement Plant Lukavac, Lukavačkih brigada bb, Lukavac, Bosnia and Herzegovina*

Article info
Received: 26/10/2018
Accepted: 18/12/2018

Keywords:
Raw Materials
Clinker
Cement
X-Ray Diffraction
Minerals

***Corresponding author:**
Đukić Duško
E-mail:duskodjukic93@gmail.com
Phone: +387 65 523- 127

Abstract: Cement is a hydraulic binder formed by the grinding process of cement clinker, as intermediate product, which is produced by baking the lime-clay raw material mixture to the sintering temperature. This research paper describes mineralogical analysis technique of primary raw materials, auxiliary components for cement production, by-product clinker and final product, cement. Used technique is X-ray diffraction technique, which is one of the most modern instrumental techniques today. Obtained results are provided in the form of diffractogram, that is used to display the mineralogical phase of components. X-ray diffraction method confirmed the theoretical knowledge of the mineralogical components of tested raw materials, clinker and cement. As expected, the main component of limestone is mineral calcite, as active compound, fly ash and slag as amorphous substances and clinker contains clinker-minerals and gyspum contains calcium sulfate dihydrate in large percentage. Main components of cement are all minerals provided in clinker and raw materials. These experiments were carried out in the Holding Company Cement Plant in Lukavac, Bosnia and Herzegovina.

INTRODUCTION

The raw materials for cement production include raw materials of carbonate character and raw material of acid character. Corrective raw materials include corrective raw materials of silicate character and corrective raw materials with high content of iron oxide.

The basic raw materials for cement production are limestone and clay. The limestone represents the dominant component, most often 75%, clay and corrective raw materials remaining 25% of the raw blend (Kostić-Gvozdenović et al., 1987). Contrary to artificially prepared raw materials, natural material containing 65-75% limestone ($CaCO_3$) and 25% clay without corrective properties (Brzaković, 2000). The limestone is a sedimentary rock composed of calcite minerals ($CaCO_3$), but also contains chemical admixtures of iron, manganese, magnesium, clay, hydrargylite, sand, organic matter, etc. (Brzaković, 2000). In addition to calcite in limestone, mineral aragonite, also calcium carbonate ($CaCO_3$), which crystallizes rhombically, can be found (Brzaković, 2000). Dolomite ($MgCO_3 \cdot CaCO_3$) can be found in limestone rocks (Brzaković, 2000). Some studies had shown that substitution of zeolite require less amount of clinker, which results in producton growth and energy savings. Therefore it reduces air pollution with decreasing the CO_2 emission and other gases as well (Canpolat et al, 2004).

Marlstone is a sedimentary rock, which is built of clay particles and calcium carbonate or dolomite (Hamzabegović, 2015). The clay content ranges from

20% to 80%, while the percentage of calcium carbonate in the form of mineral calcite ranges from 35% to 65% (Hamzabegović, 2015). The non-carbonate part in marlstone are clay minerals, such as montmorillonite, ilit, kaolinite and others.

Clay is the most widespread geological material in nature formed by the sludge diagenesis that remained at the site of the decomposition of the primary material of Pelitian origin transported with water and deposited in the aquatic environment (Hamzabegović, 2015; Pofuk, 2012). The most important clay minerals are kaolinite, hydrolysis (illite), montmorillonite.

Corrective raw materials for the production of cement are: quartz sand (SiO_2), tuffs, pyrite burns, gypsum, natural and artificial shells and melting stones. These auxiliary raw materials are added to improve cement binding properties. The auxiliary raw materials that are taken for analysis are plaster, fly ash and slag.

The main structural mineral of quartz sand is quartz, SiO_2, in interval of 90-99% (Brzaković, 2000). Quartz appears in two modifications, such as α-quartz and β-quartz.

Flying ash is produced in high temperature zones (above 1000 °C), where softening and melting of indelible mineral particles occurs, which come in the lower temperature zone (about 250°C) (Brzaković, 2000). Because of these temperature changes, fly ash acquires a glass structure and form in the form of balls or particles of irregular shape due to the effect of surface stress (Brzaković, 2000). The chemical composition of flying ash consists of the following oxides: SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, SO_3, Na_2O and K_2O (Brzaković, 2000). As for the mineralogical composition of flying ash, the basic mineral component consists of glass components and mulite ($2SiO_2 \cdot 3Al_2O_3$), with smaller quartz (SiO_2), hematite (Fe_2O_3), magnetite (Fe_2O_3, FeO), magnesite ($MgCO_3$), getite ($HFeO_2$), carbonaceous substances (Brzaković, 2000). Other minerals that can be found in the structure are given in Table 1.

Table 1. Mineral phases of fly ash (Brzaković, 2000)

Mineral phases	Chemical symbol
Corundum	Al_2O_3
Rutile	TiO_2
Wustite	FeO
Pyrite	FeS_2
Free CaO	CaO
Calcite	$CaCO_3$
Anhydrite	$CaSO_4$
Portlandite	$Ca(OH)_2$
Periclase	MgO
Brucite	$Mg(OH)_2$

The slag is also one of the corrective raw materials in portland cement production. It is a by-product obtained from the production of raw iron in high furnaces, and is formed by cooling the melting mixture of iron ore and limestone, which is added to reduce the melting temperature of iron ore.

The chemical composition of this raw material includes the Si, Al, Ca and Mg oxides. Minerals that are part of this raw material are: main mineral gelenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$), followed by minerals monocalcium silicate ($CaO \cdot SiO_2$) and dicalcium silicate ($2CaO \cdot SiO_2$) (Brzaković, 2000).

There are also crystals of olivine ($MgO \cdot FeO \cdot SiO_2$), monticellite ($CaO \cdot MgO \cdot SiO_2$), akermanite ($2CaO \cdot MgO \cdot 2SiO_2$) and calcium sulphide (CaS).

Gypsum ($CaSO_4$) is used in cement technology as an active filler. It serves as a binding component and allows quick bonding of cement, reducing the time of cement binding. It is added in the amount of 3 to 5% (Kostić-Gvozdenović et al, 1987; Brzaković, 2000).

In the clinker structure, the most important minerals are: tricalcium silicate ($3CaO \cdot SiO_2$), dicalcium silicate ($2CaO \cdot SiO_2$), tricalcium aluminate ($3CaO \cdot Al_2O_3$) and tetracaluminum alumoferite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$) (Kostić-Gvozdenović et al, 1987; Brzaković, 2000). In addition to these four main minerals, mineral monocalcium aluminate ($CaO \cdot Al_2O_3$) can also be found in the clinker structure. In order to facilitate the writing of these minerals, a system of abbreviations has been introduced, consisting of: A-Al_2O_3, C-CaO, S-SiO_2, F-Fe_2O_3.

EXPERIMENTAL

Mineralogical analysis of raw materials for cement production, analysis of clinker and analysis of portland cement as a final product were carried out with Bruker D4 Endeavor X-ray diffractometer in the Holding Plant Lukavac in Bosnia and Herzegovina. The device is very precise and serves for qualitative and quantitative determinations of all phases in one single sample, also for determining the crystal structure of the compound and for determining the phase transformations in the crystal. For this reason, it is used for various mineralogical tests, especially in the modern cement industry, where mineralogical components influence the quality and properties of cement. This device is based on the x-ray diffraction and follows Braga's law accordingly.

This device analyzes samples in liquid, solid and powder form, whether in small quantities or small in size, whether they are of an irregular shape, that they are sensitive or that they are completely powdery. The D4 diffractometer uses a modern x-ray tube using a modern X-Ray cathode containing tungsten cathode and copper anode, a CuKα = 1.5418 Å (Bruker, D4) wavelength, with an advanced LinxEye detector.

Sampling and analysis

Lime, fly ash, slag, gypsum, clinker and final product, cement, CEM I 52.5N were analyzed. Sampling of the raw material was carried out as follows: A sample of 50 g of each raw material together with four cellulose tablets, which are used as a binder supplement, were placed in the Centaurus device (manufacturer FLSmidth).

This device is very advanced in the preparation of the sample hence it combines a grinding operation with a sample pressing operation, after which the device weighs

10 g of sample and makes a pressed tablet from it, is positioned at the appropriate position in the D4 Bruker XRD instrument.

RESULTS AND DISCUSSION

The result of the mineralogical analysis of the limestone is given in Figure 1. As shown from the diffractogram, the main component is mineral calcite, as in the theoretical part stated. In smaller amount are following minerals: quartz, dolomite, illite, chlorite and pyrite. The exact number of minerals and their amounts are given in Table 2.

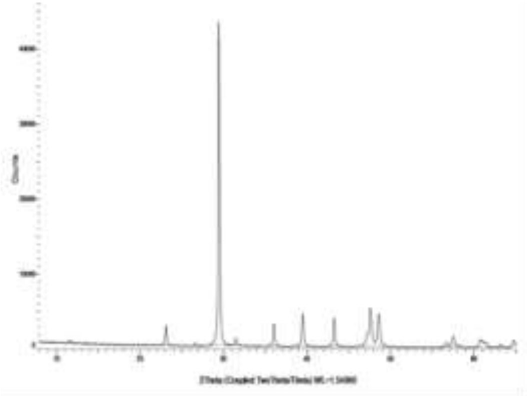

Figure 1. *Limestone diffractogram*

Table 2. Mineral phases of limestone (Vijenac, Tuzla)

Mineral phase	Amount (%)
Calcite	98.86
Dolomite	0.50
Illite	0.25
Chlorite	0.18
Quartz	0.17
Pyrite	0.03

The result of a mineralogical analysis of fly ash is given in Figure 2. Figure 2 shows that amorphous phase has largest part in this raw material, which was presumed, since this raw material does not belong to a group of rocky materials, therefore emphasize absence od crystal structure. Quartz, mulite, alite, magnetite, hematite, lime, and minor amounts of $CaCO_4$-anhydrite, tenardite, periclase and rutile are present in the following minerals. The list of mineral components and their quantity are given in Table 3.

Table 3. Mineral phases of fly ash (Tuzla Termal Power Plant)

Mineral phases	Amount (%)
Amorphous phase	61.02
Quartz	18.08
Mullite	7.34
Alite	6.46
Magnetite	2.29
Hematite	2.24
Limestone	1.28
$CaSO_4$-anhydrite	0.87
Tenardite	0.21
Periclase	0.14
Rutile	0.06

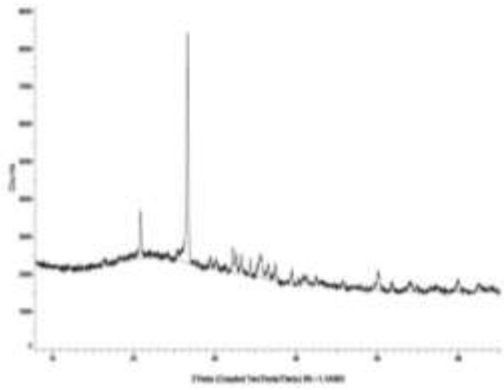

Figure 2. *Fly ash diffractogram*

The result of the mineralogical analysis of gypsum is given in Figure 3. Figure 3 shows main component of gypsum, calcium sulphate dihydrate, $CaSO_4 \cdot 2H_2O$. There is a small percentage of clay minerals, such as calcite, chlorite, illite, anhydrite, hemihydrate, magnesite and dolomite, orthoclas, quartz and thaumasite. The exact list of mineral components and mineral amounts in this gypsum sample, are given in Table 4.

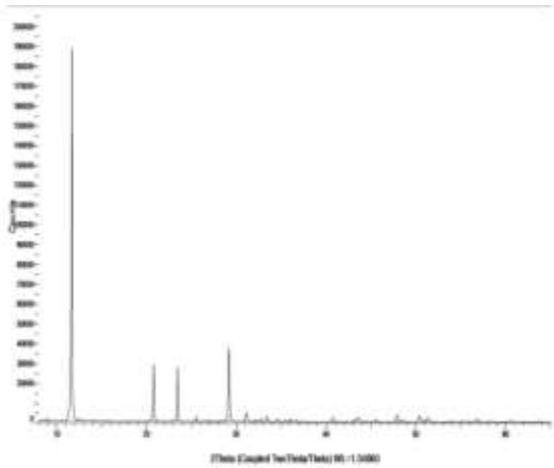

Figure 3. *Gypsum diffractogram*

Table 4. Mineral phases of gypsum (Gornji Vakuf)

Mineral phases	Amount (%)
Gypsum	92.81
Calcite	1.71
Hlorite	1.48
Illite	1.20
Anhydrite	0.59
Hemihydrate	0.58
Magnesite	0.54
Dolomite	0.51
Ortochlase	0.29
Quartz	0.15
Thaumasite	0.14

The result of a mineralogical analysis of slag is given in the next diffractogram.
The diffractogram confirmed the slag is an amorphous substance, such as fly ash (Figure 4). Minerals: bredigite, calcite and quartz are traced in this sample of slag. A list of mineral components and their respective amounts are given in Table 5.

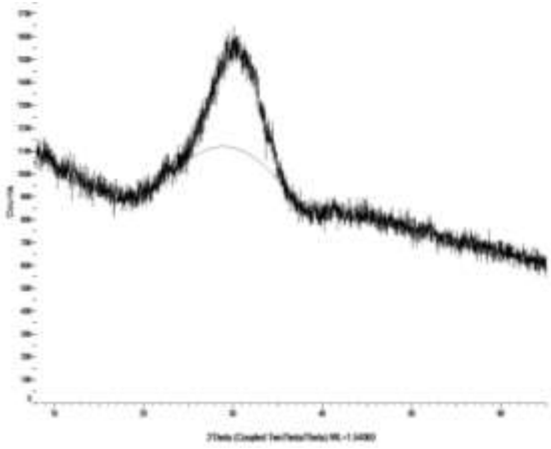

Figure 4. Slag diffractogram

Table 5. Mineral phases of slag (Zenica)

Mineral phases	Amount (%)
Amorphous phase	99.59
Bredigite	0.31
Quartz	0.06
Calcite	0.04

The result of mineralogical analysis of clinker is given in Figure 5.

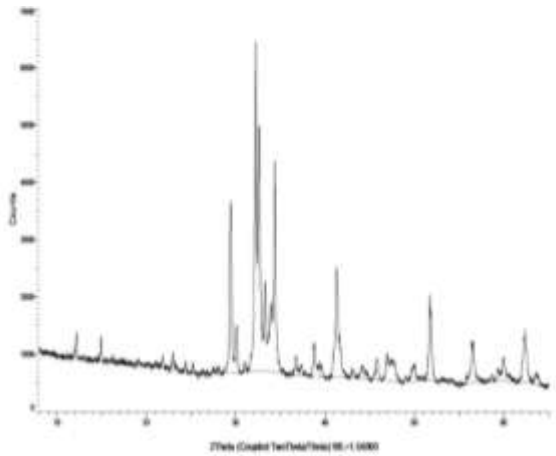

Figure 5. Clinker diffractogram

As was expected, the main components in the clinker are the main four clinker minerals: alite, belite, aluminate and ferrite. The main mineral phase is an alite with 60.86%, that 40-70% (Stutzman et al, 2004). Percentage of belite is 19.76% that corespondes to interval of 15-45%, stated to other cement studies. Figure 5 also shows amounts of aluminate and ferrite. Amount of ferrite in sample of clinker is 10.80% and amount of aluminate is 7.18%. The amounts of aluminate and ferrite coresponds to range stated in some cement studies (Stutzman et al, 2004). In this case, theoretical knowledge and research studies are confirmed. In minor amounts, other minerals are present: arcanite, free CaO, limestone, periclase, arcanite, aphtitalite and portlandite. A list of mineral components of clinker as well as their quantities are given in Table 6.

Table 6. Mineral phases of clinker (Holding Company Cement Plant Lukavac)

Mineral phases	Amount (%)
Alite	60.86
Belite	19.76
Ferrite	10.80
Aluminate	7.18
Arcanite	0.58
Free CaO	0.38
Limestone	0.32
Periclase	0.30
Aphtitalite	0.12
Portlandite	0.08

The result of a mineralogical analysis of cement is given in Figure 6. Figure 6 shows the final product, portland cement, contains in the largest amount of clinker minerals, hence cement is milled clinker. These minerals are in largest amount: alite, belite, ferrite and aluminate. In minor amounts, the following minerals are present: anhydrite, hemihydrate, arcanite, amorphous phase, portlandite, hematite, aphtitalite, quartz, magnetite and limestone. A list of mineral components and their quantities are given in Table 7.

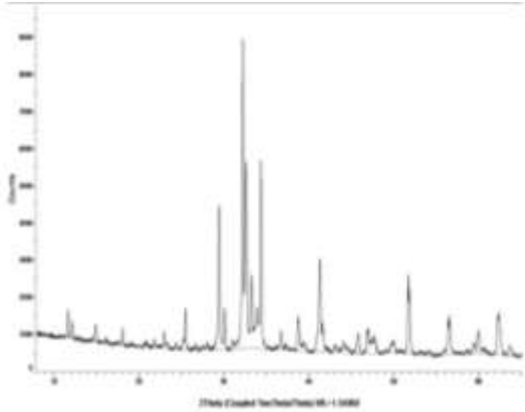

Figure 6. Cement diffractogram

Table 7. Mineral phases of cement CEM I 52.5 N (Holding Company Cement Plant Lukavac Bosnia and Herzegovina)

Mineral phases	Amount (%)
Alite	61.77
Belite	14.94
Ferrite	8.78
Aluminate	8.20
Anhydrite	1.31
Hemihydrate	1.04
Arcanite	0.79
Amorphous phase	0.72
Gypsum	0.71
Portlandite	0.57
Calcite	0.51
Free CaO	0.49
Hematite	0.39
Periclase	0.36
Aphtitalite	0.23
Quartz	0.19
Magnetite	0.14
Limestone	0.07

CONCLUSIONS

The basic raw materials for cement production are limestone and clay in, though some cement plants, such as the Lukavac cement plant do not use clay as the basic raw material but only limestone. Corrective raw materials for the production of cement are fly ash, slag, quartz sand and gypsum. Based on the analysis and the obtained results, theoretical knowledge of the mineralogical composition of the raw materials as well as clinker and cement is confirmed. In limestone from the quarry Vijenac, the main mineral is dominated by the component calcite in the amount of 98.86%, then quantities dolomite 0.50%, illite 0.25%, chlorite 0.18%, quartz 0.17% and pyrite 0.03%.

In the fly ash from Tuzla Thermal Power Plant, the main component is the amorphous phase in the amount of 61.02%, because ash does not have a crystalline structure. The largest percentage of minerals is quartz, 18.08%. The following minerals are found in smaller quantities: mullite 7.34%, alite 6.46%, magnetite 2.29%, hematite 2.24%, limestone 1.28%, anhydrite 0.87%, tenardite 0.21% periclase 0.14% and rutile 0.06%.

Gypsum is added to strengthen the binding power of cement. Gypsum, or $CaSO_4 \cdot 2H_2O$, is dominant in the structure of gypsum, in the amount of 92.81%. Other minerals found in gypsum are: calcite 1.81%, chlorite 1.48%, illite 1.20%, anhydrite 0.59%, hemihydrate 0.58%, magnesite 0.54%, dolomite 0.51% , orthoclase 0.29%, quartz 0.15% and thaumasite 0.14%.

Iron slag from Zenica as well as fly ash, is an amorphous material, in an amount of 99.59%. Other minerals that are present in slag are: bredigite 0.31%, quartz 0.06% and calcite 0.04%.

The main minerals in clinker are: alite in amount of 60.86%, followed by: belit 19.76%, ferrite 10.80% and aluminate 7.18%. Other mineral components present in clinker are: arcanite 0.58%, free CaO 0.38%, limestone 0.32%, periclase 0.30%, aphtitalite 0.12% and portlandite 0.08%.

In cement, as a final product there is a large number of minerals, which originate from raw materials and are similar in composition as in clinker. Minerals that dominate cement are clinker minerals: alite 61.77%, belite 14.94%, ferrite 8.78% and aluminate 8.20%. Other cement minerals are: anhydrite 1,31%, hemihydrate 1.04%, arcanite 0,79%, gypsum 0.71%, portlandite 0,57%, calcite 0.51%, hematite 0,39%, periclase 0.36%, aphtitalite 0.23%, quartz 0.19% and magnetite 0.14%. In the traces there is a limestone 0.07%, a smaller proportion of the amorphous phase 0.72% and a free CaO in an amount of 0.49%.

By analyzing the results of the analysis, it was found that the use of other raw materials for the production of cement, such as limestone with corrective raw materials, leads to the same mineralogical composition of cement, that is to the determination of the main clinker minerals, which are also the most important mineral components of cement.

ACKNOWLEDGEMENT

The work was conducted in Faculty of Technology Banja Luka, University of Banja Luka, Bosnia and Herzegovina and Holding Company Cement Plant Lukavac, Bosnia and Herzegovina.

REFERENCE

Bruker D4, http://www.bruker.com, (20/10/2018.)

Brzaković P. (2000). *Priručnik za proizvodnju i primjenu građevinskih materijala nemetaličnog porijekla.* Orion Art, Beograd

Canpolat F., Yilmazb K., Köse M.M., Sümer M., Yurdusev M.A. (2004). Use of zeolite, coal bottom ash and fly ash as replacement materials in cement production. *Cement and Concrete Research (34), 731–735.*

Centaurus, http://www.flsmidth.com, (20/10/2018.)

Kostić-Gvozdenović Lj. et al (1987). Inorganic chemical technology. Faculty of Technology and Metallurgy, Belgrade.

Pofuk I, *Brick clay*, seminary paper, Faculty of Chemical Engineering and Technology, University of Zagreb, Croatia, 2012.

Stutzman P. (2008). Scanning electron microscopy imaging of hydraulic cement microstructure. *Cement & Concrete Composites (26)*, 957-966.

Summary/Sažetak

Cement predstavlja hidraulično malterno vezivo koje nastaje procesom mljevenja cementnog klinkera, kao međuproizvoda, koji nastaje pečenjem sirovinske mješavine na bazi krečnjaka i gline do temperature sinterovanja. U ovom radu je opisana tehnika minerološke analize kako glavnih, tako i korektivnih sirovina za proizvodnju cementa, međuproizvoda klinkera i konačnog proizvoda, tj. cementa. Korištena je jedna od najsavremenijih instrumentalnih tehnika i to tehnika savremene rentgenske difrakcije. Rezultati analize su priloženi u vidu difraktograma, analitičkog zapisa mineroloških analize. Postupkom rentgenske difrakcije potvrđeno je teoretsko saznanje o mineroloških komponentama ispitivanih sirovina, klinkera i cementa. Kao što se i očekivalo glavna komponenata krečnjaka je mineral kalcit, elektrofilterski pepeo i troska su amorfna supstance, u klinkeru preovladavaju klinker minerali, gips sadrži dihidrat u velikom procentu. Glavne komponente u cementu su svi minerali koji su prisutni u sirovinama i klinkeru. Analize su vršene u laboratoriji Fabrike cementa Lukavac, Bosna i Hercegovina.