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Interpretation of results obtained from analyses of some raw materials for cement production, from Ribnica and Grabovica deposits

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Abstract: Basic raw materials used for portland cement clinker production are calcium, silicon, aluminium and iron oxides. In avaliable raw materials, these components are rarely found in ratio needed for clinker production. Consequently, it is important to prepare appropriate raw mixture from materials with high limestone (calcium carbonate) contents and materials with suitable contents of oxides, but with low fraction of limestone. To achieve this, it is essential to perform reliable qualitative and quantitative characterization of raw materials. In this paper, results obtained from analyses of samples used for cement production (marlstone from Ribnica and Greben quarries and marl from Greben) are presented. Chemical composition of analyzed samples is satisfactory, according to EN 197-1 standard.

INTRODUCTION

Various mineral raw materials are used in cement production, primarly limestone and marlstone followed by clay, sand, tufa, bauxite, iron ores, gypsum, etc. Some industrial wastes, such as metallurgical slag and fly ash, can also be considered as raw materials. Important factor is mineral contents needed for clinker formation or presence of some additives used in clinker production. Raw material selection depends on its availability, as well as type and desired properties of final product. Lime raw materials used for cement production are those with high content of $CaCO_3$ (40-100%) or CaO (22-56%), such as calcite, limestone and dolomite. Fraction of clay in raw material should be between 20-25 %. This component enriches basic raw material with essential quantities of acidic oxides, SiO_2, Al_2O_3 and Fe_2O_3. CaO contents in clay component is not limited, while fraction of MgO depends on its content in lime component, and should not exceed 5%. Sum of Na_2O and K_2O fractions should not be higher than 1%. Raw mixture for portland cement, which is an hydraulic binder, is composed in such manner to achieve maximum molecular saturation of acidic components (SiO_2, Al_2O_3, Fe_2O_3) with quicklime (CaO), while ensuring that there is no residual CaO in obtained clinker. Residual, chemically unbound CaO deteriorates quality of final product. Maximum content of CaO in raw material or cement is calculated from the „lime saturation factor“ equation, on the basis of percentage of acidic and basic components, obtained from chemical analysis of materials.

Best properties are obtained for cements with ratio of percentage of basic to acidic component between 1,7-2,4, i.e. in which content of basic components is two times higher than acidic components. This ratio is called hydraulic cement modulus.

Saturation factor for portland clinker varies between 90-95%. Raw materials with saturation factor between 90-98 % are considered as materials that can be calcinated without difficulties. When the saturation factor is increased, free CaO, which induce temporal instability of cement, should be considered. When the saturation factor is over 90 calcination is improved, but raw material deposits are likely to appear at the inner walls of furnace.

Raw materials with proposed hydraulic modulus, used in raw mixture for cement preparation, do not necessarily leads to quality portland cements, which are obtained if clinker contains proportions of SiO_2 to aluminum and iron oxides between 2,4 – 2,7. This value is called silica modulus and it can be used for cement quality rating.
Value of silica modulus represents the ratio of SiO_2 and sum of Al_2O_3 and Fe_2O_3 and gives ratio of calcium silicate minerals and melting minerals (calcium aluminates and calcium aluminoferites) in clinker. Cements with low values of silica modulus have higher binding rate. For more detailed quality assesment, value of alumina modulus, which represents ratio of melting minerals in clinker, is considered.
Values of alumina modulus are between 1,5 – 2,5. Alumina modulus defines composition of liquid phase in clinker. Low values are connected with low heat of hydration, slow solidification and slow binding of cement. High values of alumina modulus, together with low silicate modulus, leads to faster binding, in which case addition of gypsum is required. When the ratio of aluminium and iron oxides equals 1, alumina modulus is 0,637. In this case, only Ca_4AF (tetracalcium aluminoferrit) can be formed in clinker. This leads to formation of cement with very low heat of hydration, slow binding and negligible shrinking.

Periclase MgO

Volume staibility of cured portland cement depends, largely, on diameter of periclase (MgO) mineral phase. Clinker contains 2 % (w/w) of magnesium oxides that can be bound to clinker or can exist as free MgO. Periclase reacts with water to form $Mg(OH)_2$, in a slow reaction which continues even after all reactions that take part in solidification are finished. Volume of $Mg(OH)_2$ is higher than volume of MgO, which can lead to formation of cracks in cured cement.
When the MgO content is below 1 %, rate of cooling does not have significant impact on volume change of clinker. CaO and MgO (as periclase crystals) content should not be higher than 1 % and 5 %, respectively.

SiO_2

Nonhydraulic lime gets hydraulic properties from acidic components, and cement properties are dependent on their content. Cements with high content of SiO_2 are characterized by slow binding and hardness. High content of Al_2O_3 increases binding rate, and Fe_2O_3 makes cement resistant to corrosive chemicals.

Bases

Na_2O and K_2O react with water to form hydroxides and are a part of regular minerals used in clinker production. In contact with air, they absorb moisture and CO_2 to give carbonates. Sodium and potassium carbonates increase binding rate of cement, and they can cause adverse effects, such as fake binding. If prepared concrete is in contact with aggregate and moisture, and if alkaline content is higher than 0,6 % (given as mass of Na_2O), alkaline-silicate reaction is likely to occur.

In this work, composition of raw mixtures for portland clinker production is determined by volumetric method and X-ray fluorescence.

EXPERIMENTAL

Starting components used for preparation of raw mixtures for portland clinker were:
Marlsotne from Ribnica quarry
Marlstone from Greben quarry
Marl from Greben quarry
Pozzolan from ongoing production
Sample preparation and analysis

Marlstone and pozzolan samples are obtained automatically, in predetermined time intervals. Marlstone and marl from Ribnica and Greben quarries were sampled every twelve minutes, which gives total mass of collected sample of 5 kg per hour. Pozzolan sample is collected after grindig, but before the cyclone. Sampling is automated and performed every hour. Average sample was prepared by quartering of obtained samples, and divided on two equal parts – one for the volumetric determination of chemical composition and the other for the XRF analysis. Samples are crushed and homogenized in a laboratory mill to the specific area of 10000 cm^2/g. Tablets for XRF analysis was prepared by pressing the samples with 150 kN for 10 seconds. For XRF analysis, CubiX XRF spectrometer with Super-Q Version software was used.
Volumetric analysis of raw mixtures was performed according to EN 196-2:2005, which is current standard for this analysis.

RESULTS AND DISCUSSION

Results of chemical analysis of raw mixtures for portland cement clinker obtained with XRF and volumetric method are given in tables 1. and 2.

Table 1. *Results of chemical analysis of marlstone from Ribnica and Greben quarries*

Analyzed parameters	Marlstone, Ribnica quarry		Marlstone, Greben quarry	
	Volumetric method	XRF	Volumetric method	XRF
	Content %		Content %	
SiO_2	4,19	4,33	9,18	9,82
Al_2O_3	0,45	0,45	2,73	2,64
Fe_2O_3	0,51	0,49	2,03	1,89
CaO	52,5	52,3	46,8	46,7
MgO	0,62	0,52	0,78	0,62
K_2O	-	0,03	-	0,19
Na_2O	-	0,08	-	0,05
SO_3	0,12	0,07	0,40	0,33
Loss of ignition	41,24	-	38,00	-
Sum	99,7	-	100,0	-
Saturation factor SF	429	408,4	154,4	140,4
Hydraulic modulus HM	10,2	10,40	3,36	3,24
Silica modulus SM	4,36	6,18	1,92	2,16
Alumina modulus AM	0,88	0,43	1,34	1,39

Significant differences in composition and moduli values are obviuous for analyzed samples. Saturation factor for analyzed raw materials does not meet the requirements for portland cement. Lowest saturation factor (31,22) is obtained for marl from Greben and highest (429; 408,39) marlstone from Ribnica.

Upper limit of saturation factor, which determines maximal quantity of CaO that can be bound to acidic oxides, is 102. Thus, for raw materials with saturation factors above this limit adjustment is necessary. Presence of free CaO in cement can cause instabilities of volume, which is direct consequence of hydration of free CaO.

Another reason for preparing raw mixture with appropriate carbonate content lies in the fact that increased CaO content indicates possible release of large quantities of greenhouse gas CO_2 during the process of clinker preparation, in addition to reduced cement quality.

Marlstone samples from Ribnica quarry have highest values of silica modulus (4,36; 6,18), while samples from Greben quarry have values in the recommended limits (marlstone 1,92; 2,16; marl 2,22; 2,28). Silica modulus of pozzolan (3,02; 3,30) is slightly above the upper limit.

When silica modulus is above upper limit difficulties can occur during the calcination, which is related to the low fraction of the liquid phase and formation of higher fraction of belite. This can lead to slower binding and hardening of hydrated cement. Lowering of silica modulus leads to increased fraction of liquid phase and improves calcination of clinker.

Table 2. *Results of chemical analysis of marl from Greben quarry and pozzolan*

Analyzed parameters	Marl, Greben quarry		Pozzolan from ongoing production	
	Volumetric method	XRF	Volumetric method	XRF
	Content %		Content %	
SiO_2	27,4	27,6	13,8	13,7
Al_2O_3	8,45	8,73	3,18	2,31
Fe_2O_3	3,86	3,25	1,91	1,84
CaO	29,2	29,8	43,6	44,5
MgO	1,64	1,53	0,80	0,54
K_2O	-	0,99	-	0,29
Na_2O	-	0,04	-	0,07
SO_3	0,84	0,64	0,17	0,10
Loss of ignition	27,5	-	35,4	-
Sum	98,8	-	98,7	-
Saturation factor SF	31,2	31,7	96,8	102,5
Hydraulic modulus HM	0,73	0,75	2,32	2,49
Silica modulus SM	2,22	2,28	3,02	3,30
Alumina modulus AM	2,19	2,70	1,66	1,25

Hydraulic modulus is lowest for marl samples from Greben quarry (0,73; 0,75) and, together with the marlstone from Ribnica quarry, which have the highest values (10,2; 10,40), don't meet recommended values. These values are calculated from the results given in Table 1. and 2., because hydraulic modulus represents the rate of the lime content to the silicon, aluminium and iron oxides content.

Value of hydraulic modulus for quality cements is 2. Cements with HM < 1,7 usually don't have satisfactory strenght, while those with HM > 2,4 don't have constant volume. Raw materials with high hydraulic modulus need more heat for calcination, have higher strenght and heat of hydration, while chemical inertness is decreased.

Alumina modulus of analyzed samples in general does not meet the recommended values for portland cement, except for marl from Greben quarry. Lowest value (0,88; 0,43) was determined for marlstone sample from Ribnica quarry. This value is closest to the value at which tetracalcium aluminoferrites form (0,637). Such low value of alumina modulus is consequence of low content of aluminium and iron oxides in analyzed sample. Alumina modulus has crucial role in liquid phase formation in clinker. AM value of 0,637 means that molecular proportion of aluminium and iron oxides is 1 which, during the calcination, exclusively leads to formation of $4CaO·Al_2O_3·Fe_2O_3$ (tetracalcium aluminoferrite). Clinker obtained from this raw material can not contain $3CaO·Al_2O_3$ (tricalcium aluminate). These cements are charaterized by very low heat of hydration, slow binding and negligible shrinking. Cements with high binding rate have high values of alumina modulus and low values of silica modulus. Thus, rate of binding can be regulated by addition of gypsum.

MgO content

Presented results indicate that analyzed raw materials have low content of MgO, and his presence will not affect cement quality.

Sulfur S-SO$_3$

Sulfur is usually found in raw materials for cement clinker production, in the form of pyrite and marcasite. Also, it can enter in raw material from the fuel, during the calcination.

During the process of clinker calcination, sulfur contained in raw material and fuel converts to sulfur dioxide, which can react with fly ash and oxygen to form volatile sulfates that condense on raw material in cooler parts of furnace.

Evolution of SO_2 begins in preheating zone, where it reacts with $CaCO_3$ to form $CaSO_4$, which partially decomposes to SO_2 and CaO in calcination zone and causes increase of SO_2 in circulating gases.

Sulfates of alkaline metals in clinker improve starting hardenss of cement. However, increased sulfur content in the raw material as well as in the fuel can cause increased content of SO_2 in waste gases. For regulation of binding rate it is necessary that cement contain defined quantity of calcium sulfate, which is added as the correcting agent in portland cements. Maximum allowed content of SO_3 which will not cause sulfate swelling of cement is between 2,5 and 4 %.

Results of the analysis show that this component is far below recommended values, which implies that fuel with higher content of sulfur can be used, and that addition of gypsum can be considered.

In most cases, good agreement between results obtained by volumetric and XRF methods are obtained.

CONCLUSIONS

Analyzed samples used in cement production (marlstone from Ribnica and Greben quarries and marl from Greben) meet the recommended values according to EN 197-1, but can not be used as individual components for cement production. Preparation of appropriate raw mixtures is possible from these components.

Results also show that chemical composition of analyzed samples is well defined and that there is low content of impurities.

Raw mixtures for cement production can be prepared by mixing of appropriate quantities of particular material, with addition of corrective agents, such as iron ore (Fe_2O_3), up to the 1 % and industrial fly ash from thermoelectric plants, up to the 5 %.

Because of different composition and mass fraction of components required for portland cement production, constant analytical monitoring with calculations of required quantities of particular components for raw mixture is needed.

In general, raw mixture for cement clinker must contain 75 % of $CaCO_3$ and 25 % of other components, mainly SiO_2, Al_2O_3, Fe_2O_3. Detrimental components are MgO, K_2O, Na_2O and SO_3.

There is no significant difference between results obtained by volumetric and XPS method. Choice of method does not have impact on process monitoring and calculations of raw material quantities. However, it is crucial for time saving, as XRF method is considerably faster.

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Summary / Sažetak

Osnovne sirovine koje se koriste za proizvodnju portland cementa su kalcij, silicij, aluminij i željezo oksid. Važno je pripremiti odgovarajuću smjesu sirovina od materijala sa visokim sadržajem krečnjaka (kalcijum karbonata) i materijala sa odgovarajućim sadržajem oksida. Da bi se to postiglo, neophodno je da se izvrši pouzdana kvalitativna i kvantitativna karakterizacija sirovina. U ovom radu, dobiveni rezultati iz analize uzoraka se koriste za proizvodnju cementa (laporac iz Ribnice i kamenolom i lapora iz Grebena). Hemijski sastav analiziranih uzoraka je zadovoljavajući, u skladu sa EN 197-1 standardom.