INFLUENȚA GRADULUI DE BYPASS ASUPRA CONȚINUTULUI DE ALCALII DIN CLINCHER INFLUENCE OF BYPASS DEGREE ON THE ALKALIS CONTENT FROM CLINKER

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In the clinkerization process a negative influence on the kiln operations and the quality of clinker has the presence of volatile compounds (alkalis, sulphur, chlorine). These are brought into the system by the raw materials and fuels. At the international level an efficient method for reducing the negative effects of volatile compounds is the bypass introduction. In this paper the results of theoretical calculations of bypass revealing the influence of bypass degree on reducing of the alkali content from clinker are presented. In procesul de clincherizare o influență negativă asupra funcționării instalației de clincherizare și calității clincherului o are prezența compușilor volatili (alcalii, sulf, clor). Aceștia sunt aduși în sistem de materiile prime și combustibilii utilizați. La nivel internațional pentru reducerea efectelor negative ale compușilor volatili o metodă eficientă o reprezintă introducerea bypass-ului. In lucrare sunt prezentate rezultatele calculelor teoretice de bypass relevându-se influența gradului de bypass asupra reducerii continuțului de alcalii din clincher.

Keywords: bypass, alkali volatility, clinker, clinkerization installation, cement

1. Introduction

The researches performed at international level outlined the importance of knowledge and controlling of volatile compounds (alkali, sulphur, chlorine) because of unfavorable actions on the way in which is performed the circulation of the raw mix through clinkerization installation. When these are present in high concentrations, they determine difficulties of kiln operation through appearance of build-up in the preheater or in the kiln inlet area, the increasing of their concentration in the emissions resulted at kiln stack, respectively [1-3]. These are partially volatilized in the zone of high temperatures, recondense and form internal cycles that may influence kiln operation.-The volatile elements, such as alkali, have implications on mineralogical compounds of the clinker [2,4,5].

In order to combat negative effects of alkaline compounds, an efficient method is that of the bypass system introduction. The method consists of extraction from the kiln system of a part from the combustion gases in the point of maximum concentration of volatile compounds. An bypass system overtakes from the kiln combustion gases with the temperature of 950-1050°C, an gas flow of which size is imposed by the alkali content of the raw mix and of the volatility of alkaline compounds.

Also, if the special clinkers with low alkali content are desired, and the raw materials don't allow this thing, a solution is represented by the introduction of bypass system.

In the literature is mentioned that, because of

investment cost of the bypass arrangement and the negative influence of the bypass on energetic consumptions (heat and electrical energy) of kiln system, no more than 25% of the kiln exit gas volume is diverted through the bypass valve [3,6]. The additional consumption of heat at operation with bypass is of about 4-5 kcal/kg clinker (17-21 kJ/ kg clinker) for each percent of bypass volume. The supplementary consumption of electrical energy at the operation with bypass is about 2 KWh/t clinker, independent of the bypass volume [6,7]. In the most cases a bypass volume of about 3-10% will be sufficient [3,8]. Taking into account that the introduction of the bypass system involves the exhaustion of a quantity of dust of about 1% from raw mix, for each 10% bypass volume, is necessary founding of some solutions of its valorization. According to the literature, this dust may be valorized both as minor addition at cement grinding (as electrofilter dust), and as byproduct in other purposes (addition at obtaining of road hydraulic binders, filler for asphaltic mixtures, improvement of agriculture soils, stabilization soils/wastes, etc.) [3.9-12].

Present paper proposes to evaluate the possibility of applying the bypass system to reduce alkali content in case of using at the manufacture of Portland cement clinker usual indigenous raw materials (limestone, marl or clay).

The paper presents the results of theoretical calculations of bypass revealing the influence of bypass degree on reducing of the alkali content from clinker.

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2. Experimental data

Practical experience showed that kiln operation is made heavy, becoming often impossible, when are exceeded some limits of the concentration of volatile matters in different points of the system. Thus, in case of some clinkerization installation provided with preheater in suspension without precalcination (FLSmidth) is recommended in case of ordinary Portland clinkers as the sum of alkaline oxides (%Na₂O+%K₂O) to not exceed the value of 1.5% [13].

In the case when it follows the manufacturing of some clinkers with low alkali content is imposed a maximum limit 0.6% for alkali, expressed as Na_2O_{eq} (% $Na_2O + 0.658 \cdot \%K_2O$) [14].

Evaluation of bypass applicability in order to reduce the alkali content from clinker was performed for two distinct cases:

- case 1: using of indigenous raw materials with high alkali content for obtaining of an ordinary Portland clinker with a alkali content below recommended value of 1.5%;

- case 2: using of indigenous raw materials with lower alkali content for obtaining of a special Portland clinker with low alkali content (Na₂O_{eq} <0.6%).

For this study were used raw materials that are used in current production of cement plants. The chemical composition of these is presented in the Table 1.

Calculations of dosage in which were imposed the following modular characteristics for clinker obtaining: lime modulus $S_k=0.98$, silicate modulus $M_{Si}=2.45$ and aluminate modulus $M_{Ai}=1.45$ were performed. Calculated characteristics of the raw mix and of afferent clinkers are given in the Tables 2 and 3.

Table 1

Raw r	naterials				Chara	cteristics	Caracteri	stica, %			
Mate	rii prime	PC	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na₂O	K ₂ O	SO₃	Na ₂ O _{eq}
Case/ <i>Cazul</i>	Limestone <i>Calcar</i>	41.08	4.52	1.38	0.73	50.57	0.86	0.40	0.27	0.19	0.58
1	Marl <i>Marnă</i>	17.64	37.24	12.31	5.07	20.89	3.44	1.70	1.39	0.32	2.61
	Sand <i>Nisip</i>	5.36	84.23	1.70	1.76	4.77	0.44	1.29	0.32	0.13	1.50
	Pyrite ash Cenuşă de pirită	2.25	14.17	3.85	68.65	4.1	0.68	0.63	0.80	4.87	1.16
Case/ <i>Cazul</i>	Limestone <i>Calcar</i>	42.84	1.77	0.64	0.02	54.51	0.01	0.08	0.03	0.10	0.1
2	Clay <i>Argilă</i>	10.86	54.91	19.19	2.82	6.98	1.99	0.86	2.13	0.26	2.26
	Sand <i>Nisip</i>	6.89	83.20	2.40	0.65	4.70	0.09	0.46	1.20	0.41	1.25
	Pyrite ash Cenuşă de pirită	3.30	9.34	1.47	73.66	3.75	0.51	0.60	0.37	7.00	0.84

Chemical composition of raw materials / Compositia chimică a materiilor prime

Table

Table 2

Table 3

Calculated characteristics raw meal / Caracteristici calculate făină Oxide composition / Compoziție oxidică, % SiQ2 Al2Q3 Fe2Q3 CaQ MaQ Na2Q K2Q SQ3

	PC	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na₂O	K₂O	SO₃	Na ₂ O _{eq}
Case/ Cazul1	34.69	13.83	3.34	2.30	43.13	1.30	0.67	0.48	0.26	0.99
Case/ Cazul 2	35.05	14.02	3.39	2.34	43.74	0.32	0.25	0.57	0.32	0.63

Calculated characteristics clinker / Caracteristici calculate clincher Oxide composition / Compoziție oxidică, %

		Oxide composition / Compoziție oxidică, %												
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na₂O	K ₂ O	SO ₃	Na ₂ O+ K ₂ O	Na ₂ O _{eq}				
Case/ Cazul1	21.18	5.11	3.53	66.03	1.99	1.03	0.73	0.40	1.76	1.51				
Case/ Cazul 2	21.59	5.22	3.60	67.34	0.49	0.39	0.88	0.49	1.27	0.97				
		Mineralogical composition / Compoziție mineralogică, %												
		C₃S		C₂S	C4AF C3A				3 A					
Case/ Cazul1	68.45			9.07	10.73			7.	.59					
Case/ Cazul 2	69.80			9.25	10.95			7.	.74					

In the case 1 obtained clinker has the sum of alkaline oxides 1.76%, the value situated over the limit recommended by FLSmidth for ordinary Portland clinkers. The clinker obtained in the case 2 presents a content of Na_2O_{eq} of 0.97%, value situated over imposed limit for the clinkers with low alkali content.

In order to estimate the possibility of reducing the alkali content from clinker it was applied a simplified methodology which takes in calculation bypass degree and alkali volatility. For the calculations were used the formulas [5]:

$$K - 1 = \frac{\varepsilon_1(1 - V)}{1 - \varepsilon_2(1 - V)}$$
(1)

and

$$\Delta A = (K-1)(\frac{V}{1-V}) \tag{2}$$

where:

 $\begin{array}{l} \text{K-1} = \text{circulating alkali content;} \\ \epsilon_1 = \text{coefficient of alkali primary volatility;} \\ \epsilon_2 = \text{coefficient of alkali secondary volatility;} \\ \text{V} = \text{bypass volume ;} \\ \Delta \text{A} = \text{alkali reduction in clinker.} \end{array}$

The coefficient of primary volatility represents gravimetric proportion of the compounds that are released from the raw mix during heating in kiln, in order to pass in gases flow. Gravimetric proportion of the same compounds that are released from the material from the kiln, but resulting from their recirculation, represents the coefficient of secondary volatility [2]. In the literature are mentioned different values of volatility coefficients (ϵ_1 , ϵ_2) of alkali (Table 4).

For the calculation of reducing the content of the volatile compounds from clinker were chosen minimum and maximum values of the volatility coefficients of alkali in order to outline the importance of volatility on the alkali content from clinker (Table 5).

3. Results and discussions

In case of using indigenous raw materials with high alkali content, for obtaining an ordinary Portland clinker (**case 1**), through application the formulas (1) and (2) were obtained the results presented in the Table 6. The calculation was made separately for each alkali oxide, final expression of

Table 4

Coefficients of volatility / Coeficienți de volatilitate

Coefficient volatility/	ε ₁		ε2		
Coeficient volatilitate	Alsop [6]	Duda [5]	Alsop [6]	Duda [5]	
K ₂ O	0.67	0.4-0.6	0.88	0.9	
Na ₂ O	0.53	0.35-0.5	0.92	0.8	

Table 5

Values of volatility coefficients used in calculation / Valori ale coeficienților de volatilitate utilizați în calcul

Variant of work		ε1	ε2		
Varianta de lucru	K₂O	Na ₂ O	K₂O	Na₂O	
Α	0.4	0.35	0.9	0.8	
В	0.67	0.53	0.9	0.8	
С	0.4	0.35	0.88	0.92	
D	0.67	0.53	0.88	0.92	

Table 6

Decreasing of alkali content for ordinary Portland clinker / Reducerea continutului de alcalii pentru un clincher usual

Variant of work Varianta de lucru	% BYPASS	K-1 (K₂O)	∆A (K₂O)	K-1 (Na₂O)	∆A (Na₂O)	K₂O, %	Na₂O, %	(Na₂O+K₂O), %
A1	0	-	-	-	-	0.73	1.03	1.76
	2	3.322	0.068	1.588	0.032	0.68	1.00	1.68
	5	2.621	0.138	1.385	0.073	0.63	0.95	1.58
	10	1.895	0.211	1.125	0.125	0.58	0.90	1.48
	15	1.447	0.255	0.930	0.164	0.54	0.86	1.40
	20	1.143	0.286	0.778	0.194	0.52	0.83	1.35
	25	0.923	0.308	0.656	0.219	0.51	0.80	1.31
B1	0	-	-	-	-	0.73	1.03	1.76
	2	5.564	0.114	2.405	0.049	0.65	0.98	1.63
	5	4.390	0.231	2.098	0.110	0.56	0.92	1.48
	10	3.174	0.353	1.704	0.189	0.47	0.84	1.31
	15	2.423	0.428	1.408	0.248	0.42	0.77	1.19
	20	1.914	0.479	1.178	0.294	0.38	0.73	1.11
	25	1.546	0.515	0.994	0.331	0.35	0.69	1.04

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Table 6	6 (co	ntinu	es)
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Variant of work Varianta de lucru	% BYPASS	K-1 (K₂O)	∆A (K₂O)	K-1 (Na₂O)	∆A (Na₂O)	K2O, %	Na₂O, %	(Na₂O+K₂O), %
C1	0	-	-	-	-	0.73	1.03	1.76
	2	2.849	0.058	3.486	0.071	0.69	0.96	1.64
	5	2.317	0.122	2.639	0.139	0.64	0.89	1.53
	10	1.731	0.192	1.831	0.203	0.59	0.82	1.41
	15	1.349	0.238	1.365	0.241	0.56	0.78	1.34
	20	1.081	0.270	1.061	0.265	0.53	0.76	1.29
	25	0.882	0.294	0.847	0.282	0.52	0.74	1.25
D1	0	-	-	-	-	0.73	1.03	1.76
	2	4.772	0.097	5.278	0.108	0.66	0.92	1.58
	5	3.881	0.204	3.996	0.210	0.58	0.81	1.39
	10	2.899	0.322	2.773	0.308	0.49	0.71	1.21
	15	2.260	0.399	2.067	0.365	0.44	0.65	1.09
	20	1.811	0.453	1.606	0.402	0.40	0.62	1.02
	25	1.478	0.493	1.282	0.427	0.37	0.59	0.96

alkali concentration in clinker being made both for %Na₂O, %K₂O respectively, and as total alkali (%Na₂O+%K₂O).

In accordance with obtained data, through increasing of bypass degree from 0% up to 25%, the content of total alkali from clinker, expressed as sum of (Na_2O+K_2O) , decrease from 1.76% to 0.96...1.31% depending on the considered volatility.

For higher values of the coefficients of primary volatility (variants B1 and D1) the limit of total alkali of 1.5% in clinker is reached at bypass degree of 5%. In order to reach same limits, the decreasing with about 35% of the values for the coefficients of primary volatility involves an increasing of bypass degree at 10% (variants A1 and C1) – Figure 1.

In the situation of using indigenous raw materials with lower alkali content for obtaining a special Portland clinker with low alkali content (**case 2**) the calculation of decreasing the volatile compounds content from clinker was performed separately for Na₂O and K₂O, but the alkali content in clinker was expressed as Na₂O_{eq} (Table 7).



Fig. 1 – The content of total alkali vs bypass degree / Continutul de alcalii totale în funcție de gradul de bypass.

It is remarked that for a bypass of 50% in case when the coefficients of primary volatility have higher values – variants B2 and D2 ($\epsilon_{1Na2O}=0.53$; $\epsilon_{1K2O}=0.67$), the content of alkali expressed as Na₂O_{eq} decrease with 55% (from 0.97% to 0.43%). In case of some lower primary volatility, the variants A2 and C2 ($\epsilon_{1Na2O}=0.35$; $\epsilon_{1K2O}=0.4$), this decreasing is of only 34% (from 0.97% to 0.64%).

Table 7

Reducerea conținutului de alcalii pentru un clincher cu conținut redus de alcalii											
Variant of work <i>Varianta</i> de lucru	% BYPASS	K-1 (K₂O)	∆A (K₂O)	K-1 (Na₂O)	∆A (Na₂O)	K₂O, %	Na₂O, %	Na ₂ O _{eq} , %			
A2	0	-	-	-	-	0.88	0.39	0.97			
	2	3.322	0.068	1.588	0.032	0.82	0.38	0.92			
	5	2.621	0.138	1.385	0.073	0.76	0.36	0.86			
	15	1.447	0.255	0.930	0.164	0.66	0.33	0.76			
	20	1.143	0.286	0.778	0.194	0.63	0.31	0.73			
	25	0.923	0.308	0.656	0.219	0.61	0.30	0.71			
	50	0.364	0.364	0.292	0.292	0.56	0.28	0.65			
B2	0	-	-	-	-	0.88	0.39	0.97			
	2	5.564	0.114	2.405	0.049	0.78	0.37	0.88			
	5	4.390	0.231	2.098	0.110	0.68	0.35	0.79			
	15	2.423	0.428	1.408	0.248	0.50	0.29	0.63			
	20	1.914	0.479	1.178	0.294	0.46	0.28	0.58			
	25	1.546	0.515	0.994	0.331	0.43	0.26	0.54			
	50	0.609	0.609	0.442	0.442	0.34	0.22	0.44			

Decreasing of alkali content for a clinker with low alkali content

Variant of work Varianta de lucru	% BYPASS	K-1 (K₂O)	∆A (K₂O)	K-1 (Na₂O)	∆A (Na₂O)	K₂O, %	Na₂O, %	Na ₂ O _{eq} , %
C2	0	-	-	-	-	0.88	0.39	0.97
	2	2.849	0.058	3.486	0.071	0.83	0.36	0.91
	5	2.317	0.122	2.639	0.139	0.77	0.34	0.85
	15	1.349	0.238	1.365	0.241	0.67	0.30	0.74
	20	1.081	0.270	1.061	0.265	0.64	0.29	0.71
	25	0.882	0.294	0.847	0.282	0.62	0.28	0.69
	50	0.357	0.357	0.324	0.324	0.57	0.26	0.64
D2	0	-	-	-	-	0.88	0.39	0.97
	2	4.772	0.097	5.278	0.108	0.79	0.35	0.87
	5	3.881	0.204	3.996	0.210	0.70	0.31	0.77
	15	2.260	0.399	2.067	0.365	0.53	0.25	0.60
	20	1.811	0.453	1.606	0.402	0.48	0.23	0.55
	25	1.478	0.493	1.282	0.427	0.45	0.22	0.52
	50	0.598	0.598	0.491	0.491	0.35	0.20	0.43

In order to obtain a clinker with low alkali content (Na₂O_{eq} \leq 0.6%) in the variants B2 and D2 is necessary a bypass of 20%, 15% respectively. In the variants A2 and C2 this limit can't be reached practically (Figure 2).



In both presented cases it is stated that the necessary of bypass volume for reaching wanted limits of the total alkali content decreases with increasing of their volatility. Generally, the increasing of alkali volatility depends in high measure of operations conditions of the kiln; decreasing of sulphur input, producing of a long and stable flame, clinker burning so that CaO_{free}< 1, kiln operation with a minimum excess of air, addition of CaCl₂ [5,15,16].

4. Conclusions

In this paper were performed theoretical calculations of reducing the alkali content depending on bypass degree for two types of clinker. The calculations approved obtaining of an ordinary Portland clinker with alkali content (Na₂O+K₂O) below the limit of 1.5%, and also of a clinker with low alkali content (Na₂O_{eq} \leq 0.6%), starting from indigenous raw materials.

The results showed that higher volatility of the alkali ($\epsilon_{1Na2O}=0.53$; $\epsilon_{1K2O}=0.67$) favour the obtaining of some clinkers with alkali content below

the recommended limits using a bypass degree of: 5% in the case of ordinary Portland clinker, 15-20% respectively in case of the clinker with low alkali content. Future researches will take into account the possibilities of valorization of resulted bypass dust.

REFERENCES

- 1. G.Hu, T.Vagn Jensen, Dynamic simulation of alkali, sulphur and chloride circulation in a cement kiln, ZKG International, 2010, 63 (11), 33. *** Man
- Manualul inginerului din industria cimentului, vol II, Ed. 2. Tehnică, București, 1999, p.451.
- * European IPPC; Best available techniques (BAT) reference 3 document for the production of cement, lime and magnesium oxide - European Integrated Pollution Prevention and Control Bureau, 2013.
- A. Harrisson, Alkalis in cement, International Cement Review, 4. December 2009, 80.
- 5. M.Georgescu, G.Niculae, Impact of the alternative fuels use on the composition and on the structural characteristics of the clinkers, Romanian Journal of Materials, 2010, 40 (2), 102.
- 6 W.H.Duda, Cement - Data - Book, Wiesbaden, Berlin, 3rdEdition, 1988.
- P.A. Alsop, H.Chen, H.Tseng, The Cement Plant Operations 7 Handbook, Edition VI, 2014, edited by Tradeship Publications I td.
- J. Mullner, Successful bypass in Poland, International Cement 8. Review, January 2012, 52.
- F. Khodary, A.M. El-Kelesh, Investigation into Effectiveness of Bypass Cement Dust as Soil Stabilizer in Road Construction, International Journal of Current Engineering and Technology, 2015, **5**, (1), 519.
- 10. K. Z. Ramadan, A. M. Ashteyat, Utilization of white cement bypass dust as filler in asphalt concrete mixtures, Canadian Journal of Civil Engineering, 2009, 36 (2), 191.
- 11. A.Moanta, F.Amzica, Using cement kiln dust adition to the cement grinding, Romanian Journal of Materials, 2004, 34 (1), 36.
- 12. F. Mohsenzadeh J. Nouri, A. Ranjbar, M. Mohammadian Fazli, A. A. Babaie, Air pollution control through kiln recycling bypass dust in a cement factory, J. Environ. Health. Sci. Eng., 2006, 3 (1), .5.13. *** FLSmidth Institute, Kiln process and Operation.
- 14. *** Standard ASTM C150 / C150M 16, Standard Specification for Portland Cement.
- 15. Z.Ghizdăveţ, R.Grădinaru, A.Mustaţă, Simulation of the burning process and of the heat transfer in the flame area of the rotary kiln, Romanian Journal of Materials 2013, 43 (2), 201.
- *** Circulation Phenomena In The Clinkerization Process, 16. http://222.255.19.250/Picture/PRJ-MEC/VAN/Holcim/Circulation%20Phenomena%20in%20the%2 0Clinkerization%20Process.pdf