

# APTITUDINEA LA CLINCHERIZARE A AMESTECURILOR BRUTE VS. ACIDO-BAZICITATEA OXIZILOR COMPONENTI RAW MATERIALS' CLINKER BURNABILITY VS. OXIDES ACIDITY/BASICITY

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*Reactions that conclude to clinker formation from raw materials can be, basically, considered as taking place between oxides, and are of an acid-base nature. A straightforward hypothesis can follow: the basicity gradient between oxides – which is an intrinsic attribute of the raw meal – determines from a chemical viewpoint the raw mixes burnability. This feature, along with the Lime Saturation Factor, LSF, influences both reactions' kinetics and the degree of transformation of the reactants in reaction products. In this paper, a series of correlations between burnability and basicity gradient and LSF were extracted; in that purpose, there were used several series of foreign and indigenous raw meals. The analysis of the results confirmed the starting hypothesis.*

*Reacțiile care conduc la formarea clincherului din amestecul de materii prime au loc practic între oxizi și sunt de tipul acid-bază. Din acest motiv pare rațional să se considere că o caracteristică intrinsecă a amestecului de materii prime, precum diferența de bazicitate între oxizii componenți, determina din punct de vedere chimic, aptitudinea la clincherizare. Influența acestei caracteristici, alături de modulul de saturare în calce  $S_k$  se manifestă atât asupra vitezei de reacție între oxizi cât și asupra randamentului de transformare a reactanților în produși de reacție. În lucrare se prezintă o serie de corelații între aptitudinea la clincherizare vs. diferența de bazicitate și  $S_k$ . Rezultatele sunt obținute pentru o serie de amestecuri brute străine și românești. Ele atestă corectitudinea ipotezei de start.*

**Keywords:** clinker, raw mix, burnability, acidity and basicity, correlations .

## 1. Introduction

The aptitude of the Portland cement clinker to form is gauged by the raw meal's burnability. This is a complex parameter that is influenced by a wide variety of, both, endogenous factors (chemical, mineralogical, crystallographic features, along with the grain size distribution of the raw materials) and exogenous ones (clinkering plant's design and process control strategies).

According to scientific literature, there are various theoretical indices and a range of experimental methods to assess the burnability of the raw meal, according to its physical and chemical features. Among the experimental methods, the determination of the free CaO percentage in clinker is the most used one. Related to the value of the free CaO content, burnability can range from very low to very good (%CaO lower than 2% for a very good burnability). Theoretical approach uses indices computed by a statistical analysis of experimental data. [1-3]

In this paper it is tested the hypothesis that burnability is strongly influenced by the basicity gradient between oxides existing in the raw meal.

## 2. Theoretical background

### 2.1. Structural features

Clinkering process consists of a series of reactions that take place sequentially and/or simultaneous. Granular material transiting the clinkering plant (made of cyclones tower, calciner, rotary kiln and grate cooler) enters higher and higher temperature zones, going through, mainly: dehydration, decarbonation, solid phase reactions, clinkering, followed by, finally, clinker cooling. It is well known that if the contact time interval between hot gases – material increases, the influence of the grinding fineness and of the mineral composition in the raw meal on the burnability lessens correspondingly. As a consequence, the most important factor that influences burnability of the raw meal remains the oxide composition.

Also, it is known that reactions between reactants (oxides) are of an acid-base type, therefore they are driven by a basicity gradient. Simply put, a higher basicity gradient between reactants (though higher Gibbs free reaction energy) gives: i) an accelerated kinetics; ii) a higher transformation degree of the reactants in products. Clinkering process starts when the material begins

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to melt; the liquid phase promotes, also, diffusion processes that, at their turn, induce a faster reaction kinetics. As a consequence, more and more CaO is reacting and forms various clinker mineral compounds. Diffusion processes in the presence of the liquid phase depends on chemical composition and on the acid-base equilibrium in the liquid phase. [1, 4] In the diffusion process, the activation energy is lower for  $\text{Ca}^{2+}$  than for the  $\text{Si}^{4+}$ ,  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  ions, that are blocked in more acid and stable structural entities. As a general rule: the oxides having a higher basicity (characterized by ionic bonds and higher coordination numbers) diffuse faster than acid oxides (that have stronger covalent bonds and a smaller coordination number).

From a thermodynamic standpoint, at chemical equilibrium, the equilibrium constant at constant pressure,  $K_p$ , can be computed by the Eq. (1):

$$\ln K_p = -\frac{\Delta^{\circ}G_T^{\circ}}{RT} \quad (1)$$

with:  $-\Delta^{\circ}G_T^{\circ}$  is the free reaction energy at temperature  $T$ ;  $R$  – gases constant.

Various authors report a quantitative dependency given by a functional  $F$ , such as:

$$\Delta^{\circ}G_T^{\circ} = F(B) \quad (2)$$

where basicity  $B$  can be an „optical basicity” or a „conventional basicity” defined against the difference in electronegativity [5-7].

For a mineral compound  $aX \cdot bY$ , that can be found in cement chemistry, where  $X$  is an alkaline or alkaline earth oxide and  $Y$  can be  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$ , Radu et al. [5-7] presented models such as Eq. (3):

$$-\Delta^{\circ}G_{298}^{\circ} = (a + b) \cdot f(\Delta pB) \quad (3)$$

where  $f$  is a first/second degree polynomial,  $\Delta pB$  – basicity gradient between reactants.

We propose at that point the following hypothesis: it may be possible to exist a dependency between basicity gradient among reactants and the raw materials burnability. In order to test this hypothesis, it is necessary to identify parameters able to evaluate them; in this case, a series of theoretical indices of a chemical nature and laboratory results for free CaO will be used for burnability while basicity will be assessed by the percentage of basicity gradient.

## 2.2. Basicity assessment for oxide systems

Acidity/basicity represents a universal attribute of matter. In the particular case of oxide systems, this attribute should be considered when dealing with compounds formation and properties. In time, a series of theories were produced to argument the content of this attribute [8].

For oxide systems, qualitative arguments were supplemented by quantitative assessments only in the last 4-5 decades when Duffy et al defined „optical basicity” [9]” and Balta et al. defined „basicity percentage” [10]. Although these two theories start from different hypotheses, they

all converge to results of an identical informational content. Quantitatively, results can be deduced one from another, based on a simple functional transformation. In this paper, we used the basicity percentage,  $pB$ , to quantify oxides and oxide compounds basicity. The choice is based on the fact that Balta et al. consider that in oxide systems  $\text{O}^{2-}$  has the maximum basicity (say, 100%). Related to that value, one can define basicity percentage,  $pB$ , for other oxides by using the model of Balta and Radu [11]:

$$\lg pB = 1.9CN^{0.02} - 0.023 \frac{P_i}{CN} \quad (4)$$

with  $CN$  standing for coordination number of the cation vs. oxygen and  $P_i$  ionization energy of the cation.

For multi-compound oxide systems, basicity percentage can be computed by the equation:

$$pB = \sum_{i=1}^n c_i \cdot pB_i, \% \quad (5)$$

with  $pB_i$  standing for basicity percentage for oxide  $i$ ;  $n$  – total number of components,  $c_i$  – weight fraction of the component  $i$ .

Along with the technological workflow, the oxides constituting the materials will suffer a change of their  $pB$  only if, in one or more sequences of the workflow, processing conditions (temperature, pressure etc.) will affect the value of  $CN$ . In the same time, complex oxide systems will change basicity along the technological workflow due to various chemical reactions (dehydration, calcination etc.).

## 3. Results and discussions

### 3.1. The evolution of the basicity of the materials along the technological workflow

Along with the technological workflow, raw materials inherently change their chemical composition, through processing, and, therefore, their basicity, respectively their reactivity. For a portland cement raw mix, calcite ( $\text{CaCO}_3$ ), as a main component has a  $pB = 57.4\%$ . Amphoteric oxides  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  act as acids as related to the oxide that has the highest basicity among the raw mix, CaO. Higher basicity gradients between the oxides obtained after raw materials decomposition will yield, along with other influencing factors, higher reaction kinetics that will reduce the clinking stage to economically acceptable time levels. Close values are recorded for  $\text{Fe}_2\text{O}_3$  ( $pB = 72.5\%$ ) or  $\text{Al}_2\text{O}_3$  ( $pB = 61.6\%$ ) – for tetra-coordinated Al, as related to oxygen – and  $pB = 72.4\%$  for hexa-coordinated Al. For  $\text{Na}_2\text{CO}_3$  (as a likely supplier of  $\text{Na}_2\text{O}$ ),  $pB = 58\%$ . Kaolinite ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ) has a value in between the one of  $\text{Al}_2\text{O}_3$  and of  $\text{SiO}_2$  ( $pB = 49.4$ ). By considering a  $pB(\text{H}_2\text{O}) = 58.9\%$  and a coordination 6 of the Al in kaolinite, it results a basicity of  $pB(\text{kaolinite}) = 59.8\%$ .

Considering all of these statements, at low

Table 1

Raw materials chemical compositions (MP1, MP2) / *Compoziția chimică a amestecului de materii prime (MP1, MP2)*

Component	MP1		MP2	
	kg/100 kg cl	%	kg/100 kg cl	%
Limestone	105.87	97.24	13.13	28.12
Kaolinite	-	-	11.45	24.52
SiO <sub>2</sub>	1.82	1.67	15.86	34.01
Al <sub>2</sub> O <sub>3</sub>	0.62	0.57	2.72	5.80
Fe <sub>2</sub> O <sub>3</sub>	0.54	0.50	3.53	7.56
Σ	108.85	99.98	46.70	100.01

Table 2

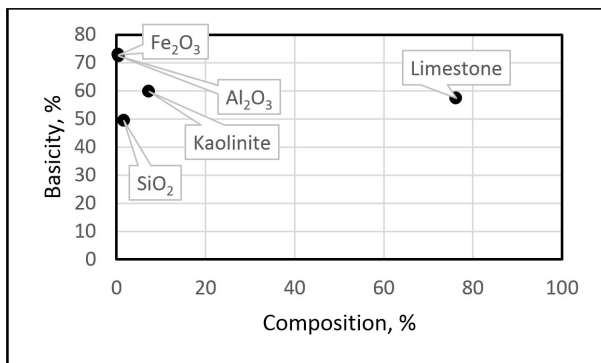
Raw mix, calcined material and clinker oxide composition / *Compoziția oxidică a făinii brute, amestecului calcinat și a clincherului*

Component	Raw mix		Calcined material		Clinker
	kg/100 kg cl	%	kg/kg cl	%	%
Limestone	119.0	76.50	-	-	
Kaolinite	11.45	7.36	-	-	
CaO	-	-	66.73	0.667	C <sub>3</sub> S = 50.82
SiO <sub>2</sub>	17.68	11.36	22.16	0.222	C <sub>2</sub> S = 25.48
Al <sub>2</sub> O <sub>3</sub>	3.34	2.15	6.64	0.066	C <sub>3</sub> A = 9.96
Fe <sub>2</sub> O <sub>3</sub>	4.07	2.61	4.52	0.045	C <sub>3</sub> AF = 13.74
Σ	155.55	99.98	100.05	1.000	100
pB, %	~57.3		~75		-

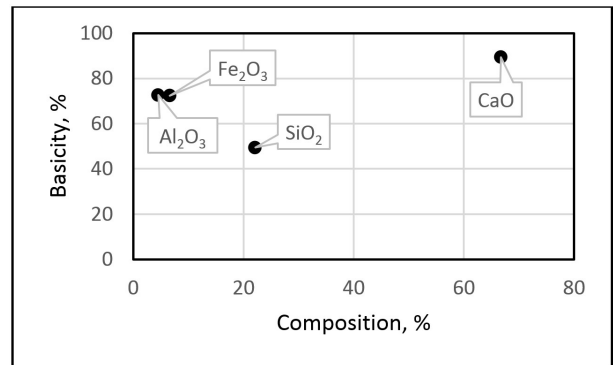
temperatures (below 300-400°C) chemical interactions (if any) between various components of the raw mix will take place very slowly, due to relatively small gradients between components' basicity. As the temperature grows higher, a series of compounds will decompose, releasing oxides that have significantly higher pB: pB(CaO) = 89.4% and pB(Na<sub>2</sub>O) = 89%. From this perspective, it clearly results that reactivity, respectively raw mix burnability, are driven by the interactions between the most basic oxide (CaO) and the more acidic oxides: SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>.

In a simplified case, we consider a clinker workflow that uses only two raw materials, MP1 and MP2. Raw materials compositions are given in Table 1. For the materials' workflow, steps are, in order, raw mix formation, calcination, clinkering; their chemical compositions are given in Table 2. Data in Table 2, correlated with the computed basicity are given in Fig. 1. Fig. 1a shows that basicity gradients for components of the raw mix are insignificant. However, Fig. 1b presents clear differences in the calcined mix between the amount and the basic attribute of the basic component and the amount and the acid attribute of the acid component. The same discussion can follow for acid mineral compounds (C<sub>3</sub>S and C<sub>2</sub>S) vs. basic

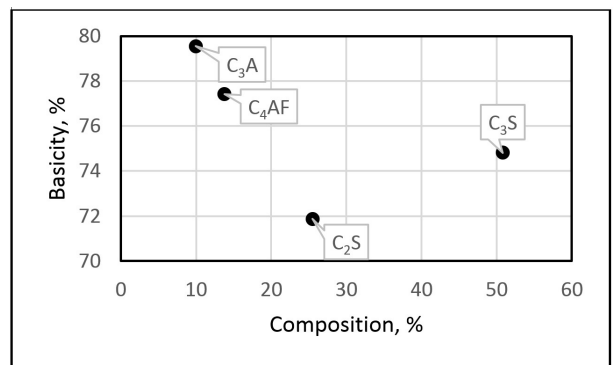
compounds of the clinker Fig. 1c. This observation can be used as a starting point for explaining some properties of the mineral compounds in clinker [12].



a



b



c

Fig. 1 - Composition and basicity of the components for: a) raw mix, b) calcined material; c) portland cement clinker / *Compoziția și bazicitatea componentelor pentru: a) amestecul de materii prime, b) amestecul de materii prime calcinat; c) clincherul de ciment Portland.*

Table 3

Oxide composition ranges of the raw mixes / Intervale de variație pentru compoziția oxidică, ale făinilor brute

%CaO	%SiO <sub>2</sub>	%Al <sub>2</sub> O <sub>3</sub>	%Fe <sub>2</sub> O <sub>3</sub>	%MgO	Σ% minor oxides	Source
42.44-44.14	13.09-14.84	2.31-4.10	1.21-4.53	0.83-0.86	0.40-0.74	[3]
41.30-43.24	12.47-14.99	2.71-4.51	1.80-5.12	0-1.94	0-1.65	[1]

$$fCaO = k_0 + k_1 \cdot \%CaO - k_2 \cdot \%SiO_2 - k_3 \cdot \%Al_2O_3 - k_4 \cdot \%Fe_2O_3 \quad (6)$$

$$fCaO = K_0 + K_1 \cdot \%CaO \cdot pB(CaO) - K_2 \cdot \%SiO_2 \cdot pB(SiO_2) - K_3 \cdot \%Al_2O_3 \cdot pB(Al_2O_3) - K_4 \cdot \%Fe_2O_3 \cdot pB(Fe_2O_3) \quad (7)$$

$$\Delta pB = 89.0 \cdot \%CaO - 49.4 \cdot \%SiO_2 - 72.4 \cdot \%Al_2O_3 - 72.5 \cdot \%Fe_2O_3 \quad (10)$$

with  $k_0, k_1, \dots, k_4$  coefficients.

Burnability, expressed as percentage of free CaO ( $fCaO$ ) in portland cement clinker, can be computed by using oxide composition [3, 12] with the aid of a statistically based Eq 6.

Equations such as (6) have been reported both for indigenous and foreign clinkers, the degree of correlation being a very strong one, i.e. between 95 and 98%. [13] Eq. (6) can be rewritten if one considers the basicity of the oxides as Eq. 7.

$$\text{with } K_i = \frac{k_i}{pB(OxO)_i}, i = 1..4$$

Eq. (7) clearly shows that burnability of an industrial raw mix, assessed by measuring the free CaO, is strongly correlated with the basicity gradient between the basic and the acid component(s), such as:

$$\Delta pB = \%B \cdot pB(B) - \sum \%A_i \cdot pB(A_i) \quad (8)$$

with  $\%B$  – percentage in the basic component ( $\%CaO$ );  $\%A_i$  – percentage in the acid component  $i$ ; ( $\%SiO_2, \%Al_2O_3, \%Fe_2O_3$  etc.);  $pB()$  – basicity percentage for the basic/acid components.

In the next Results and discussions Section, it was intended to extract possible functional dependencies between burnability and  $\Delta pB$ , for a series of indigenous and foreign clinkers that had information about their oxide composition and  $fCaO$ .

#### 4. Results and discussions

26 foreign laboratory raw mixes [3] and 7 industrial Romanian raw mixes, coming from different cement plants [1], were investigated. Oxide composition,  $x_i$ , in %, of the raw mixes is given in Table 3, for the main oxides. Oxide composition of the calcined raw mixes and of clinkers,  $X_i$ , were computed by using the loss on ignition,  $PC_i$ , by Eq:

$$X_i = 100 \frac{x_i}{100 - PC_i} [\%] \quad (9)$$

Basicity gradient  $\Delta pB$  between basic and acid components of the raw mix was computed with the Eq 10

In a first approach, a series of correlations were obtained between various theoretical indices and  $\Delta pB$ . For the group of 26 foreign raw mixes, results are plotted in Fig. 6-10. Their analysis shows that:

- burnability values, expressed with the aid of the indices BI (*Burnability Index*), BF (*Burnability*

*Factor*) and IR (*Refractory Index*) are smaller; higher values of  $\Delta pB$  give optimal levels for burnability (Fig. 2-4);

- according to Fig. 5, 7, clinker heat of reaction  $Q_r$  decreases with the increase of  $\Delta pB$ , which reflects a better clinkering capacity;

- Fig. 6 presents an expected, logical result: percentage of liquid phase  $P_{liq}$  increases with the basicity gradient; the consequence is a higher burnability;

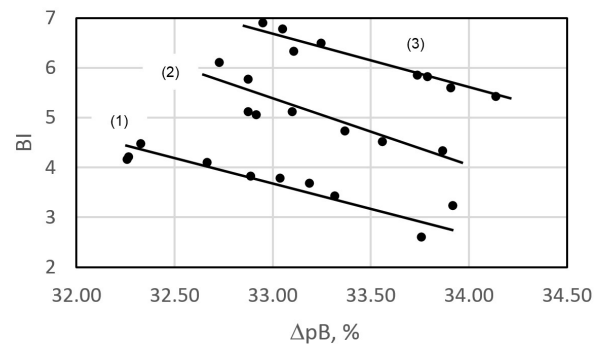


Fig. 2 - Correlations BI vs.  $\Delta pB$  / Corelația BI vs.  $\Delta pB$ .

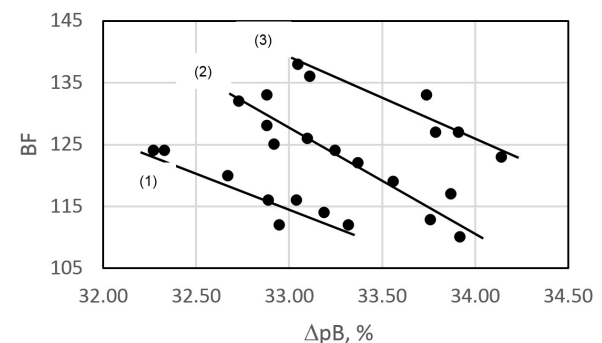


Fig. 3 - Correlations BF vs.  $\Delta pB$  / Corelația BF vs.  $\Delta pB$ .

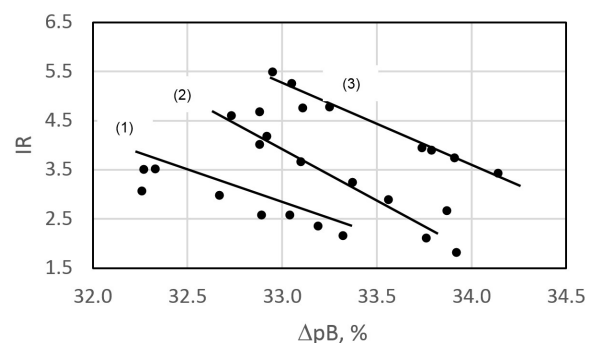


Fig. 4 - Correlations IR vs.  $\Delta pB$  / Corelația IR vs.  $\Delta pB$ .

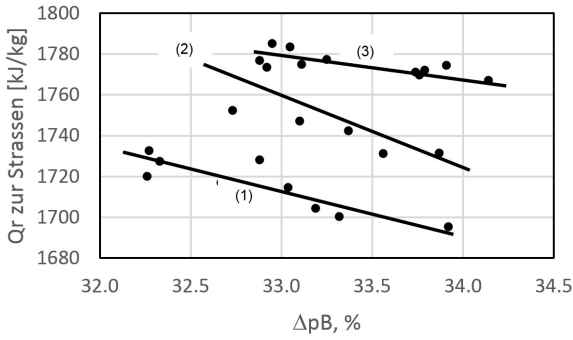


Fig. 5 - Correlations  $Q_r$  (zur Strassen) vs.  $\Delta pB$  / Corelația  $Q_r$  (zur Strassen) vs.  $\Delta pB$ .

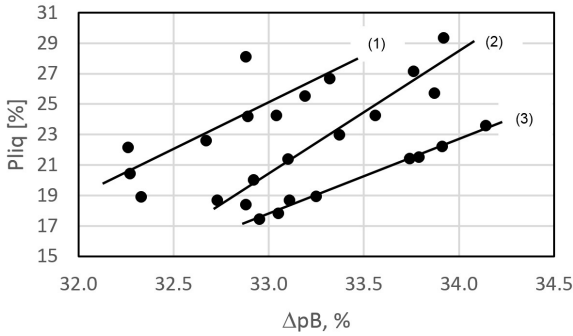


Fig. 6 - Correlations  $P_{liq}$  vs.  $\Delta pB$  / Corelația  $P_{liq}$  vs.  $\Delta pB$ .

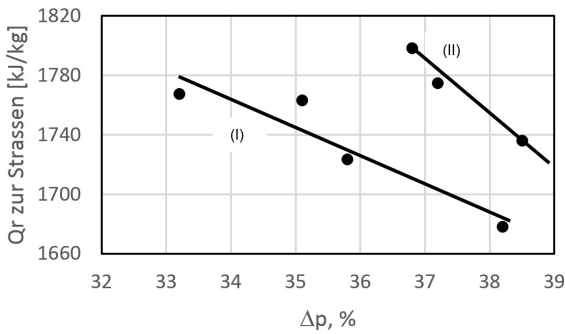


Fig. 7 - Correlations  $Q_r$  (zur Strassen) vs.  $\Delta pB$  (indigenous raw meals) / Corelația  $Q_r$  (zur Strassen) vs.  $\Delta pB$  (făini românești).

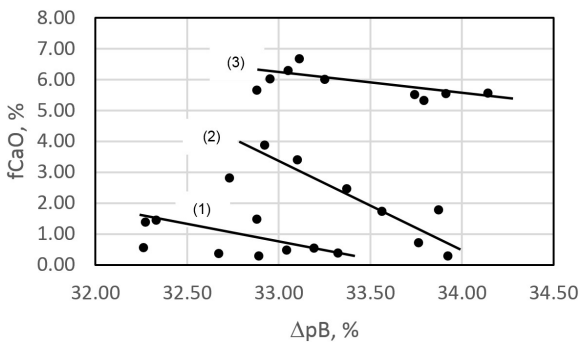


Fig. 8 - Correlations  $fCaO$  vs.  $\Delta pB$  (foreign raw meals) / Corelația  $fCaO$  vs.  $\Delta pB$  (făini străine).

- in all cases it arises obviously that there is an another important index, along with  $\Delta pB$ , that influences raw mix burnability and that index is the LSF. According to the value of the LSF, the 26 raw mixes were clearly clustered without any intervention for: (1)  $LSF \cong 95\%$ , (2)  $LSF \cong 100\%$ , (3)  $LSF \cong 105\%$ . From all charts it resulted that for the

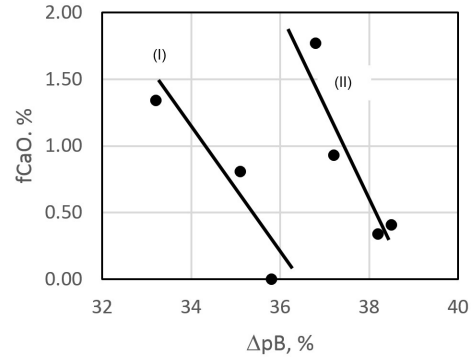


Fig. 9 - Correlation  $fCaO$  vs.  $\Delta pB$  (indigenous raw meals) / Corelația  $fCaO$  vs.  $\Delta pB$  (făini românești).

same value of the  $\Delta pB$  the mixes that present higher values of the LSF show a lower burnability. For a qualitative standpoint this result had to be expected; however, the statistical analysis of the data provides functional dependencies of the type: theoretical index for the burnability vs.  $\Delta pB$ ,  $S_k$ , dependencies that offer quantitative results.

For indigenous, Romanian, raw mixes, the relatively low number of data yielded charts in which the analysis becomes less secure. However, it has to be observed, in Fig. 7, the dependency of the theoretical heat of reaction  $Q_r$  with  $\Delta pB$  and LSF (I -  $LSF \cong 93\%$ , II -  $LSF \cong 96\%$ ). Conclusions are consistent with the ones referring to chart in Fig. 5.

The second approach consisted of investigating the existence of some dependencies between experimental values used to evaluate burnability, given by  $fCaO$  in clinkers, and  $\Delta pB$ . Fig. 8 shows the dependency  $fCaO$  in percentage, vs.  $\Delta pB$  and LSF for laboratory made raw mixes. Fig. 9 provides the same correlations for Romanian raw mixes. Both figures prove in a quantitative manner what has to be expected from the theoretical analysis; raw mixes of higher  $\Delta pB$  values and lower LSF are easier to be subjected to clinkering.

### 5. Conclusions

In this paper it was suggested and demonstrated the hypothesis that, clinker raw materials' burnability is influenced by basicity gradients between oxide reactants (components of the raw mix). In that purpose, clear and strong correlations between theoretical/experimental indices of burnability and basicity gradient were identified. In all cases, it was observed that optimal ranges for all theoretical indices but also for experimental ( $fCaO$ ) correspond to higher values for  $\Delta pB$ .

Also, in all cases, it was observed (by a simple visual analysis), that data points were grouped unsupervised (without any intervention) in well-defined clusters, according to the values of LSF (higher LSF value give the raw mix a weaker

burnability). It can be concluded, therefore, that burnability (for example, expressed as %fCaO), depends simultaneously on  $\Delta pB$  and  $LSF$ . This observation can be useful in the optimal design of the oxide composition of the clinker and of the raw mix.

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