

RELAȚII ÎNTRE INDICATORII TEORETICI DE EVALUARE A APTITUDINII LA ARDERE A AMESTECULUI DE MATERII PRIME PENTRU OBȚINEREA CLINCHERULUI

RELATIONSHIPS BETWEEN BURNABILITY INDICES OF THE RAW MIX FOR CLINKER PRODUCTION

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Nowadays clinker processing technology has been, already, reached the highest performance level that can be attained in industry. No significant improvements of a constructive/functional type of the present day's best clinkering plants can be foreseen in the next future. As a consequence, further fuel savings can be obtained by, only, a proper selection of the raw materials that require less heat in order to obtain clinker. The evaluation of the burnability of the raw mix, either by computing or experimentally, provides the most valuable information from both scientific and industrial viewpoints. In this paper, we briefly analyze existing theoretical indices used for evaluating burnability; afterwards, we explore the possible interrelations among them. In that purpose, a comprehensive database of 119 raw mixes from both industry and laboratories, from Romania and abroad were used in this investigation.

Tehnologia actuală de obținere a clincherului a atins, deja, nivelul maxim de performanță pentru indicatorii tehnico-economici caracteristici pentru instalațiile cele mai moderne, iar schimbări semnificative de tip constructiv-funcțional nu se întrevăd în viitorul apropiat. În acest context, economii suplimentare de combustibili se mai pot obține doar prin alegerea unor materii prime care să necesite furnizarea unei cantități minime de căldură necesară pentru obținerea clincherului. Pentru aceasta, evaluarea aptitudinii la ardere a amestecurilor brute, experimental sau teoretic, oferă informațiile cele mai valoroase atât din punct de vedere științific cât și practic, industrial. În lucrare se prezintă pe scurt indicatorii teoretici cei mai uzitați în acest scop și se investighează existența unor posibile inter-relații. Au fost folosite în acest scop un număr de 119 amestecuri de laborator și industriale, din țară sau din străinătate.

Keywords: clinker, burnability, correlations

1. Introduction

Portland cement clinkering process is a very complex physicochemical one. It is characterized by a large number of interconnected process parameters. These parameters influence the rate of two clinkering steps (Fig. 1) [1]:

- obtaining the oxides in a solid state by thermal decomposition (up to temperatures of about 950-1000°C); thus the "reactivity" of the raw materials mixture is defined, with particular reference to obtaining CaO by thermal decomposition of calcite;

- initiating and completing the reactions between oxides (with or without the participation of the liquid phase), with an advanced bonding of CaO; on this basis the "burnability" of raw materials mixture is defined [2-4].

Through time, several ways to assess raw materials burnability have been reported in literature. This can be done through theoretical or experimentally determined indices. Whatever the

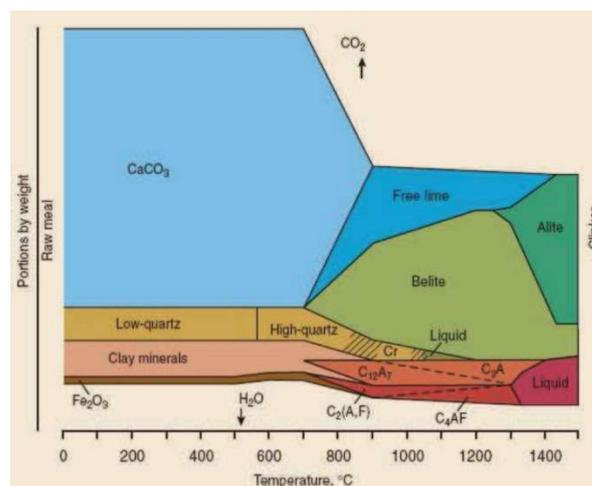


Fig. 1 - Temperature dependent transformation of minerals into clinker [1]/Transformarea mineralelor în clincher în funcție de temperatură [1].

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definition of these indices might be, in the end they show different nominal values, depending on the criteria used.

This paper makes an assessment of the correlation degree between different groups of indices defined in literature. In this purpose, information collected on raw meals/cements from six sources is used.

2. Theoretical considerations

2.1. Burnability evaluation

The evaluation of the burnability of raw materials can be done based on experimental analysis as well as by calculating some theoretical indices.

A relatively wide variety of experimental methods for assessing burnability is available, such as: sulfuric acid dissolution method, for assessing silica in solution, thermal analysis methods and the method of determining the free CaO, denoted $fCaO$. Obviously, in each case, a particular evaluation scale is being used. Even with the evaluation method based on measuring $fCaO$, there are various types of thermal treatment (time - temperature regime) [2-5].

Calculation formulas are defined in relation to:

- Chemical composition;
- Indices concerning grain size distribution;
- Curing temperature.

Therefore, the indices that can be used in assessing the burnability can be grouped into three main classes:

I. Theoretical indices that are computed only on the basis of experimental chemical composition in various ways:

- I.1 – based on oxides;
- I.2 - based on moduli;
- I.3 - compared to mineralogical constituents;
- I.4 - mixed relationships;

II. Indices calculated based on chemical composition and some experimental data referring to, for example, certain particle sizes describing the grain size distribution;

III. Experimental methods for direct assessment of $fCaO$, as a final criterion regarding the practical level of burnability.

In this paper there are used Equations belonging to the first class, respectively that compute the burnability of the mixture.

2.1.1. Indices expressed by the oxide composition

The heat of reaction, Q_r , and the percentage of liquid phase, P_{liq} , belong to this class of indices.

- Heat of reaction Q_r , after zur Strassen (1).
- The heat of reaction, Q_r , after Onoda (2).

Equations used in the paper

$$Q_r = (4,11 Al_2O_3 + 6,48 MgO + 7,646 CaO - 5,116 SiO_2 - 0,59 Fe_2O_3) \times 4.18 \left[\frac{kJ}{kg} \right] \quad (1)$$

$$Q_r = (4,8 Al_2O_3 + 7,14 CaO + 5,87 MgO - 73) \times 4.18 \left[\frac{kJ}{kg} \right] \quad (2)$$

$$P_{liq} = 3Al_2O_3 + 2,25 Fe_2O_3 + MgO + Na_2O + K_2O \quad [\%] \quad (3)$$

$$I = 0.5 LSF + 5 MSi - \frac{20}{MAL} \quad (4) \quad \%Al_2O_3 = \frac{a \times MH}{MH+1} \quad (7)$$

$$\%CaO = \frac{a \times MH}{MH+1} \quad (5) \quad \%Fe_2O_3 = \frac{a}{(MSi+1)(MH+1)(MAL+1)} \quad (8)$$

$$\%SiO_2 = \frac{a \times MSi}{(MSi+1)(MH+1)} \quad (6)$$

$$Q_r = \left(\frac{MAL}{(MAL+1)(MSi+1)(MH+1)} + \frac{7.64MH}{MH+1} - \frac{5.116 \cdot MSi}{(MAL+1)(MH+1)} - \frac{0.59}{(MAL+1)(MSi+1)(MH+1)} + 6.48 \cdot m_c + Q_{al} + Q_{sc} \right) \cdot 4.18, \quad (9)$$

$$Q_r = f(HM, MSi, MAL, MgO) \quad (10)$$

$$Q_r = \left((100 - \%MgO) \frac{7.14 \times MH (MSi+1)(MAL+1) + 4.89 \times MAL}{(MH+1)(MSi+1)(MAL+1)} + 5.87 \times \%MgO - 73 \right) \cdot 4.18 [kJ/kg \text{ cl}] \quad (11)$$

$$Q_r = (115 \cdot HM + 10 \cdot Al - 25 \cdot MSi + 225) \cdot 4.18 [kJ/kg \text{ cl}] \quad (12)$$

$$Q_r = (2.4 \cdot S_k + 10 \cdot MAL - 25 \cdot Si + 235) \cdot 4.18 [kJ/kg \text{ cl.}] \quad (13)$$

$$BI = \frac{C_3S}{C_4AF + C_3A} \quad (14) \quad R = \frac{C_3S + 0.6 C_3A - 0.61 C_4AF}{1.12 C_3A + 1.45 C_4AF} \quad (15)$$

$$T_{clin} = 1300 + 4.51 \cdot C_3S - 3.74 \cdot C_3A - 12.64 \cdot C_4A \quad (16)$$

$$\%CaO = 0.74 \cdot \%C_3S + 0.65 \cdot \%C_2S + 0.62 \cdot \%C_3A + 0.46 \cdot \%C_4AF \quad (17)$$

$$\%SiO_2 = 0.26 \cdot \%C_3S + 0.35 \cdot \%C_2S \quad (18) \quad \%Al_2O_3 = 0.38 \cdot \%C_3A + 0.21 \cdot \%C_4AF \quad (19)$$

$$\%Fe_2O_3 = 0.33 \cdot \%C_4AF \quad (20)$$

$$\%C_3S = 4.07 \cdot \frac{HM}{HM+1} - \frac{7.6 \cdot MSi(MAL+1) + 6.72 \cdot MAL + 1.42}{(MSi+1)(HM+1)(MAL+1)} \quad (21)$$

$$\%C_2S = -3.05 \cdot \frac{HM}{HM+1} + \frac{8.6 \cdot MSi(MAL+1) + 5.06 \cdot MAL + 1.07}{(MSi+1)(HM+1)(MAL+1)} \quad (22)$$

$$\%C_3A = \frac{2.65 \cdot MAL - .69}{(MSi+1)(HM+1)(MAL+1)} \quad (23)$$

$$\%C_4AF = \frac{3.04}{(MSi+1)(HM+1)(MAL+1)} \quad (24)$$

$$LSF = \frac{0.74 \cdot \%C_3S + 0.65 \cdot \%C_2S + 0.62 \cdot \%C_3A + 0.46 \cdot \%C_4AF}{0.74 \cdot \%C_3S + 0.98 \cdot \%C_2S + 0.42 \cdot \%C_3A + 0.46 \cdot \%C_4AF} \quad (25)$$

$$MSi = \frac{\%C_3S + 1.33 \cdot \%C_2S}{1.44 \%C_3A + 2.05 \cdot \%C_4AF} \quad (26)$$

$$MAL = \frac{1.15 \%C_3A}{\%C_4AF} + 0.64 \quad (27)$$

$$HM = \frac{0.74 \cdot \%C_3S + 0.65 \cdot \%C_2S + 0.62 \cdot \%C_3A + 0.46 \cdot \%C_4AF}{0.26 \cdot \%C_3S + 0.35 \cdot \%C_2S + 0.38 \cdot \%C_3A + 0.54 \cdot \%C_4AF} \quad (28)$$

$$BF = LSF + 10 MSi - 3 \times (MgO + Alkaline oxides) \quad (29)$$

$$Q_r = (5.284 \cdot \%C_3S + 4.641 \cdot \%C_2S + 6.285 \cdot \%C_3A + 4.311 \cdot \%C_4AF + 5.87 \cdot \%MgO - 73) \cdot 4.1868 \quad [kJ/kg cl.] \quad (30)$$

$$P_{liq} = 1.13 \cdot C_3A + 1.35 \cdot C_4AF + MgO + Na_2O + K_2O \quad (31)$$

For higher values of the heat of reaction, a lower burnability has to be expected.

To assess the percentage of liquid phase at 1450°C, the following Eq. can be used (3) [3].

In industry, the values of P_{liq} vary between 20-40%. The method does not indicate the optimal value for this one; however, a higher percentage of liquid phase indicates a higher burnability of the raw materials.

2.1.2. Indices expressed depending on the moduli

Typically, in Portland cement chemistry the following moduli are used [2, 3]:

- Lime saturation factor LSF (Kühl).
- Hydraulic moduli HM .
- Silica moduli MSi .
- Alumina moduli M_{Al} .

LSF is intimately related with the proportion of free lime, C_2S and C_3S . An increase in LSF causes an increase in the burning temperature and consequently an increase in the energy consumed. MSi determines the relation between the calcium silicate and the sum of the clinker interstitial matrix and is also related to the development of the liquid phase. A high value for MSi decreases the burnability of the raw meal. M_{Al} controls the composition and nature of the liquid phase. The higher the M_{Al} , the higher should be the curing temperature [5].

An indices of the burnability could be considered I (Humpola) (4) [6].

It can be anticipated that the raw mixtures characterized by higher values of I will be harder to burn.

In addition, considering the equations of definition of the moduli as a linear system of 4 x 4 equations, the oxide composition can be described in relation to the considered moduli (5 – 8). Let:

$a = \%CaO + \%SiO_2 + \%Fe_2O_3 + \%Al_2O_3$. The oxide composition depending on the moduli (5-8):

For a quaternary system, the value of a is 100. If the clinker also contains other oxides (MgO , Na_2O , K_2O ...), a has values less than 100.

Eqs. (9) - (12) allow the relations in which the indices depending on the oxide composition can be reformulated in relation to the moduli. Thus, the theoretical heat of reaction required to form clinker can be calculated based on three moduli or by LSF and two moduli, the general relation being (9).

If $\sum(\%CaO, \%SiO_2, \%Fe_2O_3, \%Al_2O_3, \%MgO) = 100$, Q_r is obtained according to the moduli composition (10, 11).

The fundamental Eq. (10) can also be expressed in simple, empirical forms (12-13).

At that moment, the following conclusions can be drawn:

- Both LSF and theoretical heat of reaction depend mostly on the value of the hydraulic module. A change of 0.1 for the HM value determines a variation of about 4.5% for LSF and approximately 48-54 kJ/kg cl. for Q_r .
- Changing the silica moduli by ± 0.2 implies (for $HM = \text{constant}$ and $M_{Al} = \text{constant}$) that LSF modifies by $\pm 1\%$ and the theoretical heat of reaction by ± 24 kJ/kg cl.
- It is also highlighted that an increase in the alumina moduli from 1.8 to 2 influences LSF very little in the range shown for HM and MSi , and the theoretical heat of reaction by only 4-5 kJ/kg cl.

Logically, an increase of the theoretical heat of reaction reflects a lower burnability.

2.1.3. Indices expressed by mineralogical constituents

In industrial practice it has been found that the ability to form clinker is well evidenced by:

- The burnability index BI (14).
- If: - $BI < 2.6$ – easier to burn mixtures;
- $BI > 4.2$ – harder to burn mixtures.
- The refractory index, IR (15).

If $IR = 1.3 \div 3.0$ it is considered that the raw meal has a normal burnability.

- The clinkering temperature, T_{clin} (16)

Higher values for T_{clin} indicate a harder to burn mix.

Starting from Bogue's equations [2] for calculating clinker minerals, one can express them as being dependent on the oxide composition or moduli. Expressing the oxide composition based on the mineralogical composition leads to (17-20).

Expressing the mineralogical constituents depending on the moduli leads to (21-24):

Expressing the moduli depending on the mineralogical constituents leads to (25 - 28).

Concluding, all indices used to assess the burnability in relation to the chemical composition of the mixtures can be expressed according to a convenient reference frame.

2.1.4 Mixed equations

This category includes a number of indices such as:

- Burnability factor, which also takes into account the influence of minor oxides like MgO and alkaline oxides calculated using the formula (29) [3, 4].

Increasing the burnability leads to a harder burning of the raw material mixture.

By using equations (17) and (19) in equation (2) one can obtain the heat of reaction (according to ONODA), this time depending on the mineralogical composition at equilibrium (30).

The percentage of liquid phase P_{liq} , after Lea and Desch's formula, at 1450°C can be computed by Eq. (31).

The higher the percentage of liquid, the easier the burning for the raw material mixture.

3. Results and discussions

3.1. To highlight the degree of correlation between various theoretical indices, but also between these and experimental data of $fCaO$, 6 sets of raw materials were used:

- 3 sets of raw industrial mixtures S1-S3;
- 3 sets, S4-S6, representing mixtures taken from literature.

In Table 1 it is shown the oxide composition C_{1i} where $i = 1..8$ for the 8 mixtures which form the S1 set, as well as the measured values for $fCaO$ determined on the resulted clinkers. Table 2 indicates the oxide composition C_{2j} where $j = 1..11$ - for 11 industrial cements (S2 set). Table 3 indicates 12 local mixtures forming set S3, characterized by a modular composition and experimentally determined values for $fCaO$ [7]. Set 4 is made of 19 industrial raw meals. They are characterized by the oxide composition, and the burnability via $fCaO$ analysis. [6] Set 5 provides the same information as set S4, but the analysis is done on 29 synthetic raw meals [6]. Finally, set 6 groups 40 oxide compositions for the analyzed clinkers [8].

For populations that make up each data set S1...S6, the most important theoretical burnability assessment indices were calculated, as well as any possible correlations between them. In cases where $fCaO$ data were available, interrelations between that information and the computed indices were investigated

Table 1

The oxide composition of 8 industrial raw mixtures (set S1) and $fCaO$ of resulted clinkers
Compoziția oxidică a 8 amestecuri brute industriale (setul S1 de valori) și $fCaO$ din clincherule rezultate

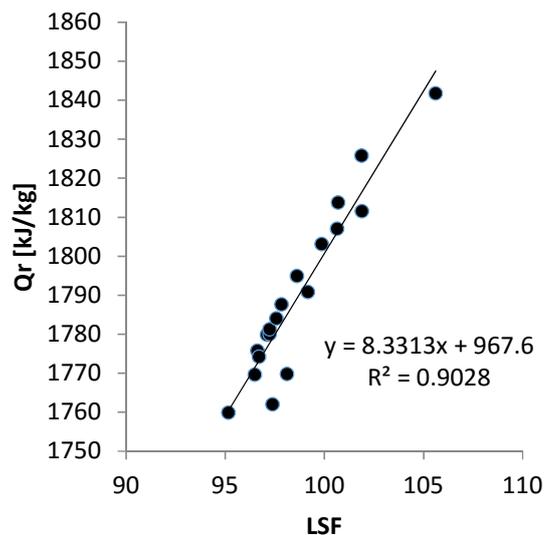
Oxide	C _{1.1}	C _{1.2}	C _{1.3}	C _{1.4}	C _{1.5}	C _{1.6}	C _{1.7}	C _{1.8}
SiO ₂ (s)	13.4	13.94	13.40	14.63	13.63	12.88	12.47	14.99
Al ₂ O ₃ (a)	3.16	2.81	4.24	4.36	4.28	4.38	4.51	2.71
Fe ₂ O ₃ (f)	2.42	2.48	2.60	1.80	2.55	2.83	5.12	2.42
CaO(c)	43.63	42.6	41.3	41.90	42.90	43	41.97	43.24
MgO(m)	1.38	0.69	1.94	0.98	0.40	0.85	1.09	0.00
K ₂ O(k)	0.43	0.70	1.00	0.79	0.97	0.00	0.70	0.60
Na ₂ O(n)	0.81	0.95	0.47	0.25	0.16	0.00	0.19	0.50
PC	35.14	35.14	34.54	34.72	34.65	33.71	33.75	34.23
fCaO	2.89	0.41	0.81	0.00	0.93	1.77	1.34	0.34

* Note: The oxide composition X_i of the clinker is calculated based on the oxide composition x_i and the loss on ignition pc_i of the raw meal: $X_i = 100 \cdot x_i / (100 - pc_i)$ / Notă: Compoziția oxidică X_i a clincherului se calculează în funcție de compoziția oxidică x_i și pierderea la calcinare pc_i a făinii brute: $X_i = 100 \cdot x_i / (100 - pc_i)$.

Table 2

The oxide composition for some industrial clinkers (set S2)/
Compoziția oxidică pentru o serie de clinchere industriale (setul S2)

Composition	c	s	a	f	m
C _{2.1}	64.18	21.58	5.85	3.89	4.50
C _{2.2}	66.28	22.31	5.54	2.81	3.06
C _{2.3}	64.11	22.56	6.63	3.81	2.89
C _{2.4}	65.60	23.26	6.72	2.91	1.51
C _{2.5}	66.91	23.24	6.28	2.65	0.92
C _{2.6}	65.94	23.11	4.83	2.89	3.23
C _{2.7}	65.06	22.35	6.35	4.30	1.94
C _{2.8}	66.67	23.61	6.99	2.03	0.70
C _{2.9}	64.28	21.41	5.67	3.32	5.32
C _{2.10}	64.82	22.11	6.96	4.84	1.27
C _{2.11}	67.00	23.65	5.35	2.47	1.53

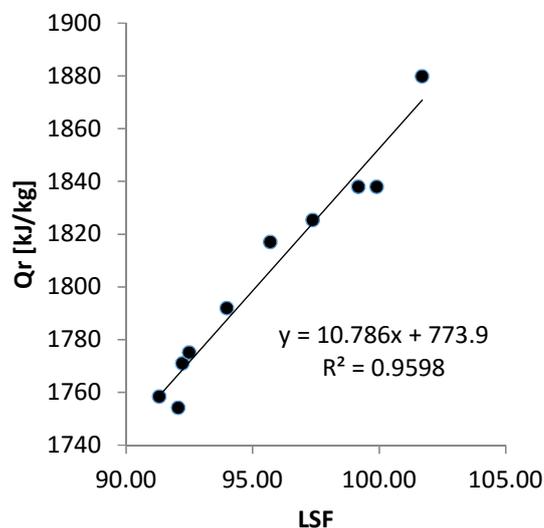


a

Table 3

The moduli composition of the raw mixtures and fCaO for the corresponding clinker (set S3)/Compoziția modulară a amestecurilor brute și fCaO (setul S3)

Composition	LSF	M _{Si}	M _{Al}	fCaO
C _{3.1}	91.31	2.14	1.92	1.40
C _{3.2}	92.06	2.20	2.23	2.87
C _{3.3}	92.23	2.32	2.38	6.18
C _{3.4}	92.49	2.34	2.24	4.09
C _{3.5}	93.98	2.31	2.47	3.85
C _{3.6}	95.69	2.32	2.40	4.30
C _{3.7}	97.37	2.25	2.38	3.02
C _{3.8}	98.34	1.72	1.50	4.46
C _{3.9}	99.18	2.17	2.14	3.21
C _{3.10}	99.67	1.77	1.09	3.87
C _{3.11}	99.90	2.34	2.39	7.51
C _{3.12}	101.70	2.32	2.19	4.09



b

Fig. 2 - Correlation Q_r vs. LSF for data from source S4 - (a) and S3 - (b)/ Corelația Q_r vs. LSF în cazul datelor din sursa S4 - (a) și S3 - (b).

3.2. Correlations between theoretical burnability indices

In this first approach, the calculation of the following indices belonging to different classes was taken into account: LSF and HM ; P_{liq} and Q_r ; IR , BI and BF . A simple statistical analysis on these data revealed a number of dependencies between variables, each having a different R^2 coefficient.

For the beginning, correlations between a series of indices with elaborate mathematical expressions and some of the moduli were studied. Of all of these, the most important was considered LSF which was selected as the independent parameter. The strongest correlations were recorded for the heat of reaction Q_r , considering S4

set ($R^2 = 0.90$) – Figure 2.a. A similar result is also obtained for S3 ($R^2 = 0.96$) - Figure 2.b.

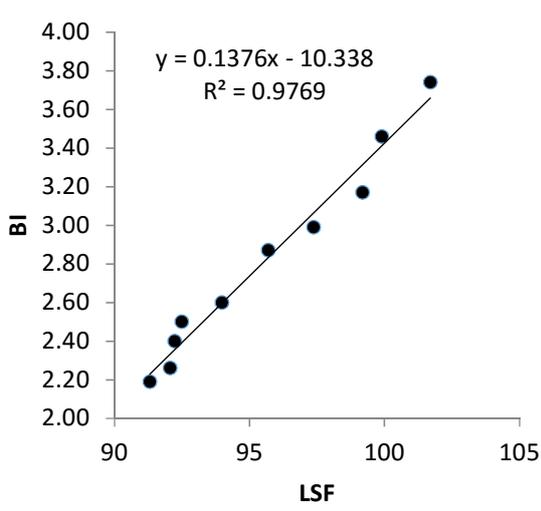
For other cases, weaker correlations were recorded ($R^2 < 0.8$, for example for S5).

At the same time, comparing BI , BF and IR data to LSF highlights:

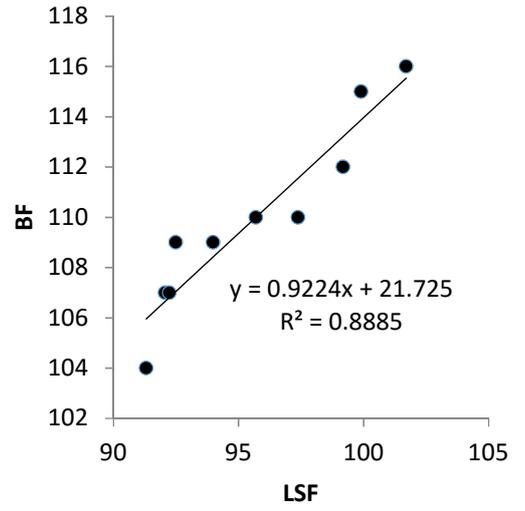
- A strong correlation, for the system S3, Figure 3 a-c, wherein $R^2 > 0.95$, less for BF vs. LSF ; such high values for R^2 are recorded for IR vs. HM , when $R^2 = 0.98$ for system S2.

- A moderate correlation between variables, with R^2 values around 0.75; (S4), Figure 3, d-f.

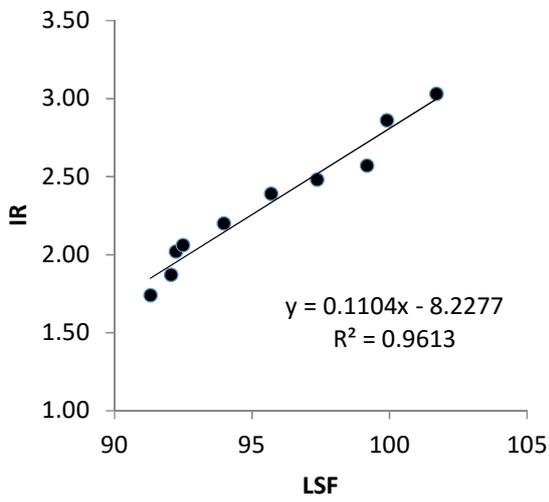
- A very low interdependence, characterized by values of $R^2 < 0.75$, in case of system S5.



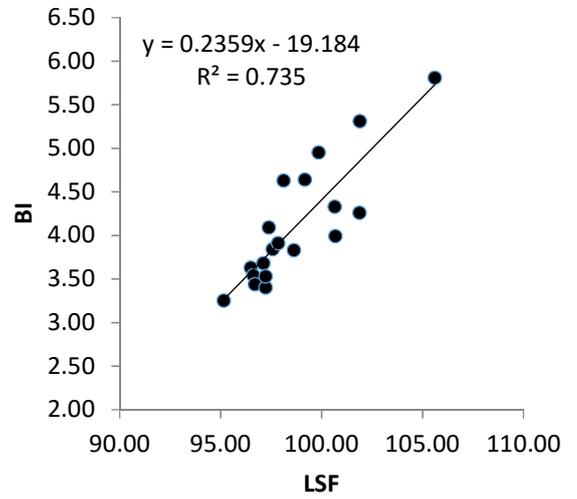
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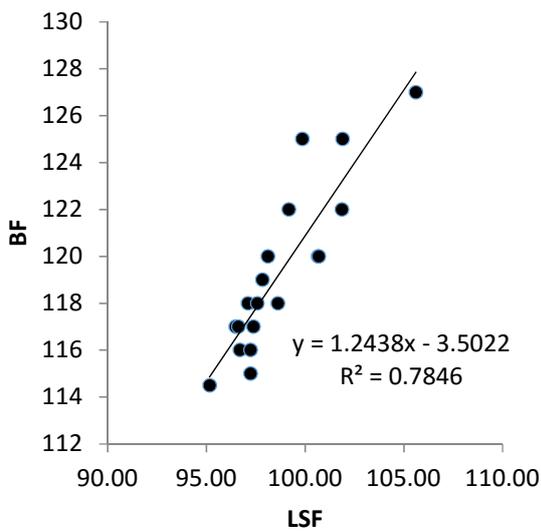
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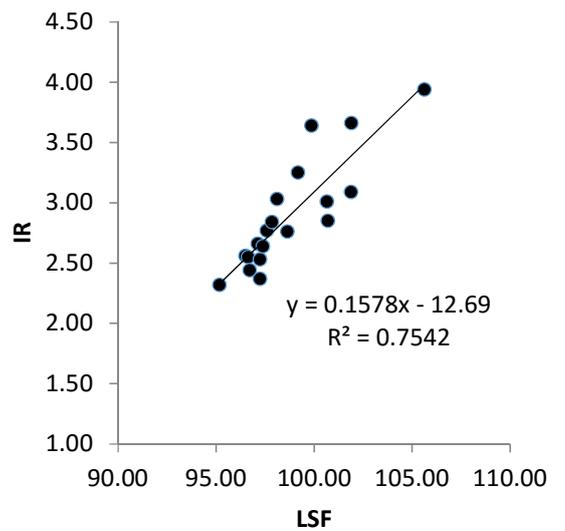
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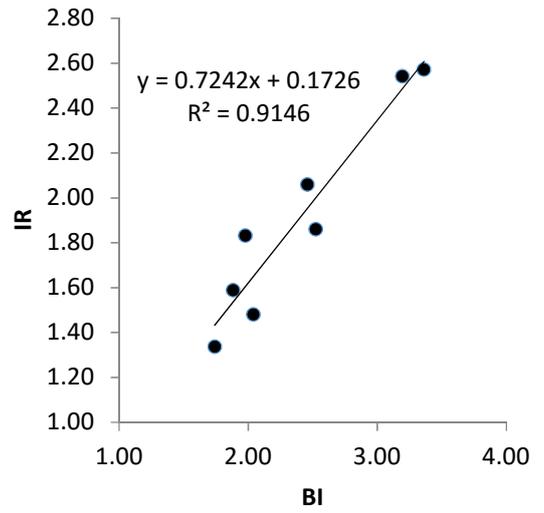
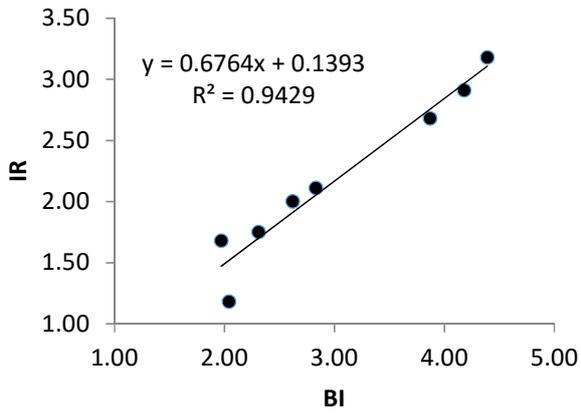


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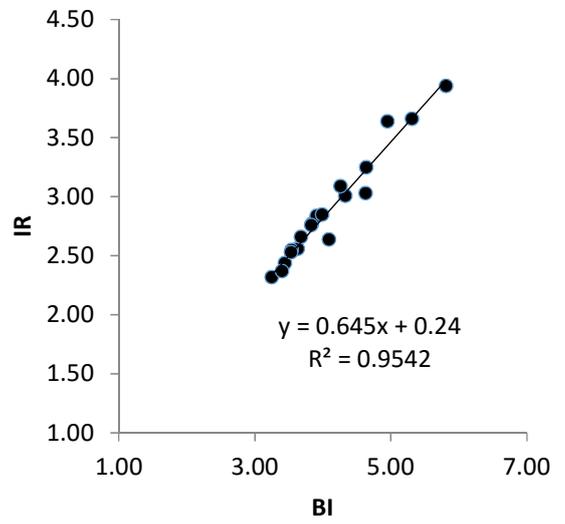
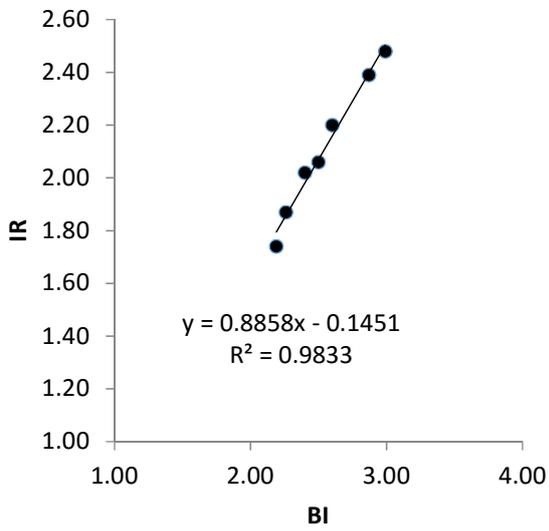
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Fig. 3 - Correlation BI, BF and IR vs. LSF for systems S3, S4 / Corelația BI, BF și IR vs. LSF pentru sistemele S3, S4.



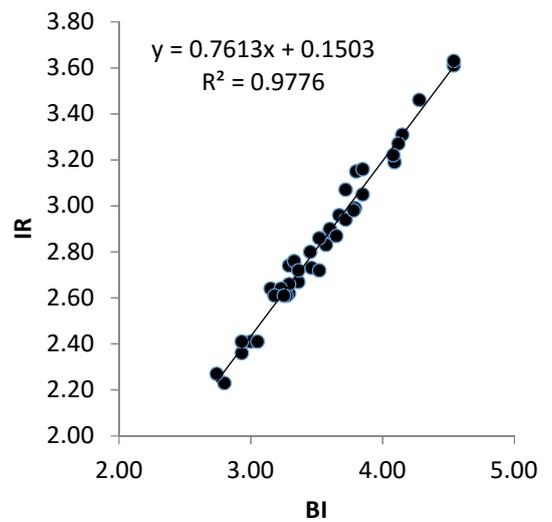
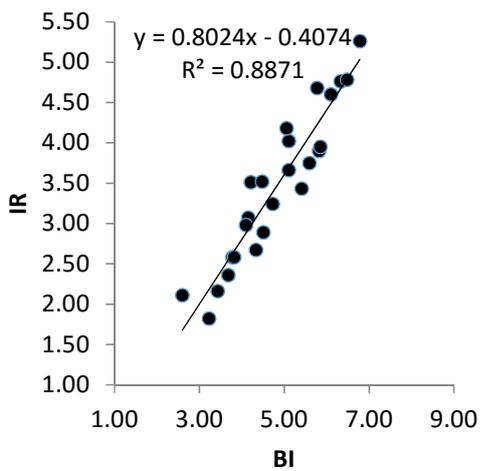
a

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c

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f

Fig. 4- IR vs. BI correlations based on data from the sources S1, S2, ..., S6, with (a), (b), (c), (d), (e), (f), respectively / Corelații IR vs. BI pe baza datelor din sursele S1, S2, ..., S6, respectiv (a), (b), (c), (d), (e), (f).

Table 4

R² coefficient for variables Q_r vs. BI, BF or IR / Coeficienții de corelare R² pentru funcțiile liniare Q_r vs. BI, BF sau IR

Source S	S1	S2	S3	S4	S5	S6
Indices						
BI	<0.1	<0.6	0.96	0.49	0.89	-
BF	<0.1	<0.6	0.85	0.66	0.78	-
IR	<0.1	0.74	0.95	0.60	0.86	-
Obs.	-	-	Fig. 5	-	Fig. 6	Not analyzed

For S1 data system, the burnability indices BI, BF and IR show a good correlation with LSF and Q_r (R² < 0.86). The same indices, relative to P_{liq}, reveal, for example, a relatively moderate-good correlation for the data from source S5 - Figures 4 a, b, c, R² ∈ [0.66-0.89], or lower, with R² ∈ [0.58-0.72] for the case S1, Figures 4 e, f, g. In case S4, in all three correlations, R² ≤ 0.37.

The correlation analysis results between the heat of reaction Q_r and indices BI, BF and IR are shown in Table 4.

For all data sources, S1-S6, the highest values of R² were obtained for IR vs. BI dependence, as shown in fig. 4. The correlation type is linear where y=IR and x=BI.

The IR vs. BF dependencies are shown in Figure 5 for data from S4 source that gave the best fit.

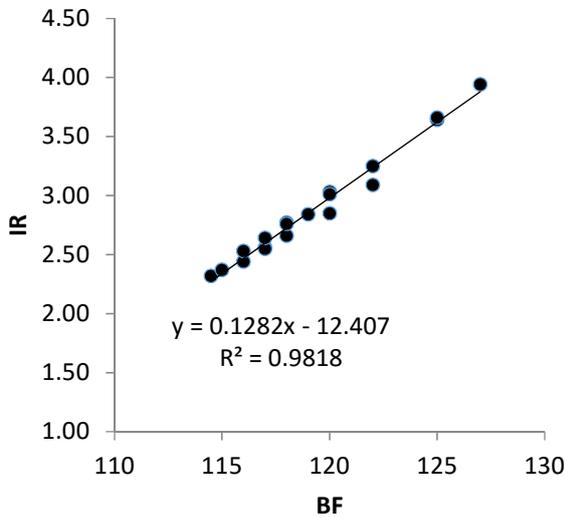


Fig. 5. - IR vs. BF correlations on the basis of data from source S4 / Corelația IR vs. BF pe baza datelor din sursa S4

Note that in the case S4, Figure 5, there is a high degree of correlation, R² = 0.98, while in 3 cases, based on S1, S3 and S5 data, R² values are in the range [0.8 - 0.9]. In the case of sources S2 and S6, the correlation between variables IR and BF is very low, R² < 0.6. As a consequence, the same types of correlations resulted for variables BF and BI.

All theoretical indices showed different correlation degrees between them, from very low to very high, depending on the case. However, in all cases, R² higher than 0.9 were recorded only for IR vs BI correlations. Good correlations of R² higher than 0.8 were recorded in many cases involving Q_r or P_{liq} vs. IR, BI, BF or HM, LSF.

3.3. Correlations between experimentally determined indices and theoretical indices

It is to be expected that the burnability can be obtained accurately, experimentally. However, the literature presents a whole series of experimental methods for determining the burnability and fCaO, respectively [2-5]. Unfortunately, these methods cannot be compared with those obtained on the basis of different methodologies. For example, the Holderbank test for evaluating burnability, B_H is as follows:

- B_H = - very good, if %fCaO ∈ [0-2%]
- good, if %fCaO ∈ [2-4%]
- average, if %fCaO ∈ [4-6%]
- weak, if %fCaO ∈ [6-8%]
- very weak, if %fCaO > 8%

At the same time, the index proposed by Blaise computed by the fCaO content in materials processed at different temperatures for 20min [3] can be used to express burnability B_B as following:

Table 5

The correlation degree for fCaO vs theoretical indices of burnability evaluation / Gradul de corelare fCaO vs indicii teoretici de evaluare a aptitudinii la ardere

Theoretical indices	BF Eq. (28)	BI Eq. (14)	T(Ludwig) Eq (5)	I(Humple) Eq (5)	U ₁ Eq. (32)	U ₂ Eq. (3)
Correlation coefficient						
R ²	0.74	0.65	0.90	0.07	0.96	0.94

- B_B= - very good, if A_C ∈ [1.00-1.50];
- good, if A_C ∈ [1.50-2.00];
- average, if A_C ∈ [2.00-2.50];
- weak, if A_C > 2.50.

In this context it is interesting to identify any correlations between the experimentally determined values of *fCaO* and various theoretical indices calculated on the basis of the chemical composition of the raw mixtures. Such an approach can be found in a detailed study carried out by Vega and Roviroso [6] in which they are looking for possible correlations between *fCaO* content (determined through the author's method) and various indices that express burnability, based on the analysis of 29 synthetic raw meals and 19 industrial raw meals. In all cases, between *fCaO* and indices related to the burnability *I_C*, linear relationships of dependency were considered. Table 5 shows the correlation coefficient R² between the variables for the 6 cases.

Indexes U₁ and U₂ are defined as following:

$$U_1 = 2.18 \cdot \%CaO - 2.48 \cdot \%SiO_2 - 0.70 \cdot \%Fe_2O_3 - 1.19 \cdot \%Al_2O_3 - 50.97 \quad (32)$$

$$U_2 = 0.500 \cdot LSF + 1.075 \cdot M_{Si} + 0.126 \cdot M_{Al} - 50.450 \quad (33)$$

A possible correlation between *fCaO* and various theoretical indices that express the ability to form clinker was investigated. The analysis of data from S4 and S5 and partly S6 is presented in Table 6.

Table 6

The correlation degree (R²) between *fCaO* and a number of physico-chemical characteristics of the systems/ Gradul de corelare (R²) între *fCaO* și o serie de indicatori de ardere teoretici

Index \ Source	LSF	P _{liq}	Q _r	BI	IR	BF
S4	0.92	0.57	0.76	0.85	0.85	0.87
S5	0.87	0.32	0.81	0.82	0.69	0.66
S6	-	-	-	0.83	0.71	0.45

Partly, some data presented in Table 6 is confirmed from other sources as well. For example, *fCaO* vs LSF has R² = 0.77, and *fCaO*-Q_r is characterized by R²=0.91, in case S1, according to the plot in Figure 6.

Note that in S1 case, *fCaO* is not correlated with BI, BF, IR and P_{liq}, resulting from statistical analysis that R²<0.1. Low values for the correlation factor are recorded for the dependence *fCaO* vs P_{liq} and for data from source S3 (R² = 0.549), S4 and S5 (see table 5). However, for the data set S5 a relatively good R² factor (R² = 0.81) is registered, which measures the correlation degree between *fCaO* and Q_r (Fig. 7).

These plots attest that in some cases, linear dependencies may be obtained statistically between *fCaO* and theoretical burnability indices. However, the values for R² are higher than 0.80 and little are

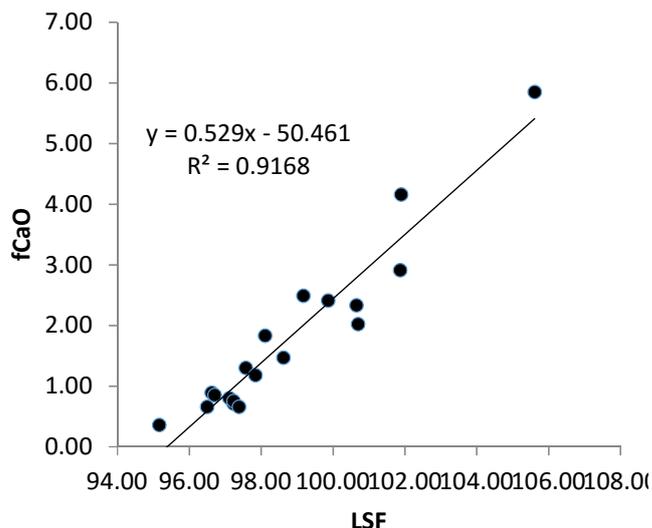


Fig. 6 - *fCaO* vs LSF dependence for data from S4 / Dependenta *fCaO* vs LSF pentru datele din sistemul S4.

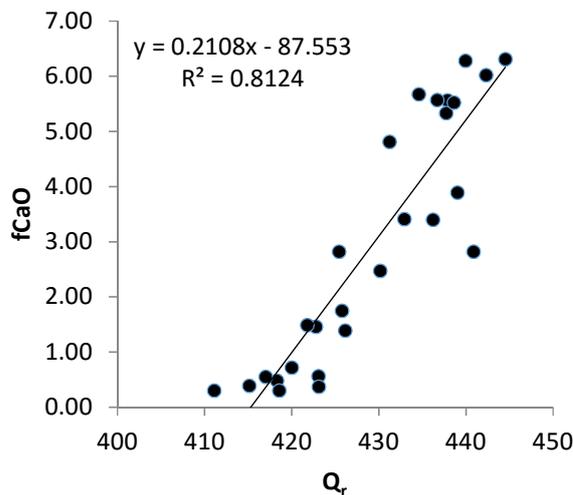


Fig. 7 - *fCaO* vs Q_r dependency for data from system S5/Dependenta *fCaO* vs Q_r pentru datele din sistemul S5

over 0.90. The explanation is that different methods of determination of *fCaO* lead to different values [9]. Also, grain size distribution, particles shape, even the presence of impurities affects the burnability of the raw mixtures [1, 2, 4, 9, 10].

Literature points out that the effect of the fineness and of the composition of the raw mix is becoming less important with the increase of the temperature and burning time. For this reason, in order to evaluate burnability of some industrial raw mixes taking into account only the chemical composition, it was obtained a mathematical equation:

$$fCaO = k_0 + k_1 \cdot CaO - k_2 \cdot SiO_2 - k_3 \cdot Al_2O_3 - k_4 \cdot Fe_2O_3 \quad (34)$$

where k₁-k₄ represent coefficients. The total correlation coefficient of the equation is 0.98 [9].

Experimental studies have shown that a number of minor components (ZnO, CuO, BaO) can exist in the raw mix, usually up to 3%. Their presence affects burnability by changing clinkering temperature, by affecting the formation of some minerals and the kinetics of some crystallization processes [10-12].

4. Conclusions

12 theoretical indices that describe raw mix burnability were analyzed in this paper. They were successfully used to describe a comprehensive database made of 119 raw mixes coming from industry or laboratory, from Romania and abroad. Examples given here can help to select the most appropriate index according to particular needs.

It was pinpointed that, even though they have different definitions, these indices can be expressed – by simple algebraic transformation – only by using the oxide composition/moduli/minerals. As a consequence, one can easily assess and compare the burnability of different raw mixes by using these simple models, with the aim of selecting the best raw mix.

A statistical approach on the correlation coefficient between different pairs of indices revealed that they reached, in many cases, high R^2 values.

For further work, other influences such as grain size distribution, processing conditions, type of elementary cell (for the crystalline phase), the presence of some other chemical components etc. should, also, have to be considered.

REFERENCES

1. P. C. Hewlett, *Lea's Chemistry of Cement and Concrete*, 4th edition, Arnold Publishers, London, Great British, 1998
2. I. Teoreanu, *Basics in Technology of Inorganic Binders*, Ed. Didactical and Pedagogical Publishing house, Bucharest, 1993.
3. xxx, *The Handbook of the Engineer in Cement Industry*, Vol 2, Technical publishing house, Bucharest, 1999.
4. A. Krahner, J. Kicsér, B. Gathemann, *Correlations between raw mix specific parameters and its reactivity to clinker burning*, *Materiale de Constructii*, 1985, **15**(2), 106.
5. G. Kakali, E. Chaniotakis, S.Tsivilis, E. Danassis, *Differential Scanning Calorimetry, A useful tool for prediction of the reactivity of cement raw meal*, *J. of Thermal Analysis*, **52**, 1998, 871.
6. J.R.A. Vega, M.L. Rovirosa, *Caracterization de diversos indices de aptitud a la coccion de crudo para fabrication de clinker*, *Cemento-Hormigon*, 1994, 261.
7. M. Toader, L. Dobronauteanu, M. Mosor, *Evaluation possibilities of the bruning aptitude of the raw mix used in clinker production*, 5th NCB International seminar of cement and building materials, XII-62, XX-69
8. L.P. Stojkanovic, *Correlation between raw materials composition and quality of portland cement*, *Proceedings of 12th Conference on Glass and Ceramics*, Varna, 453-458 Sept. 24-26, 1996
9. A. Toader, E. Nedelescu, E. Rădulescu, D. Radu, *Cement industry raw mixes burning aptitude. Quantitative correlations*, *CONSILOX VII*, Constanta, 60-66, 1996,
10. G. Kakali, G. Parisakis, D. Bouras, *A study of the burnability and the phase formation of PC clinker containing Cu Oxide*, *Cement and Concrete Research*, 1996, **26**(10), 1473-1478
11. G. Kakali, G. Parisakis, *Investigation of the effect of Zn oxide on the formation of portland cement clinker*, *Cement and Concrete Research*, 1995, **25**(1), 79.
12. A. Moanță, V. Fugaru, R. Trușcă, M. Gheorghe, M. Coarnă, I. Petre, *Research regarding obtaining of the clinkers designed for performing cements with capacity of radiations attenuation*. *Romanian Journal of Materials*, 2015, **45**(1), 21.



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