CALCULUL COMPOZIȚIEI OXIDICE OPTIME A CLINCHERELOR ÎN FUNCȚIE ȘI DE APTITUDINEA LA CLINCHERIZARE A AMESTECURILOR BRUTE
OPTIMAL OXIDE COMPOSITION COMPUTATION BY INTEGRATING RAW MATERIALS' CLINKER BURNABILITY

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Clinker minerals are of the outmost importance as they are responsible for final product's performance, i.e. cement's performance. Experimental are the best way to achieve accurate results as concerning the optimal clinker composition but they become expensive when exploring a large searching space. Mathematical optimization programing techniques, used here, can help to reduce the amount of experiments. An additional benefit is that such computational techniques can incorporate, as it is shown here, various technological and/or thermo-technical constraints. In this paper, raw materials' burnability and the oxides basicity weight played a decisive role along with other, supplementary constraints.

Compoziția mineralogică a clincherului are o importanță majoră în determinarea performanțelor acestuia, inclusiv a produsului final, cimentul. Abordarea experimentală reprezintă calea cea mai potrivită pentru a obține compoziția mineralogică optimă însă aceasta devine prohibitivă atunci când spațiul de căutare a soluției este mare. În această direcție, tehnicile de programare matematică optimală, folosite în acest articol, pot ajuta la reducerea volumului experimental. Un beneficiu suplimentar al utilizării acestor tehnici computaționale este că acestea pot încorpora, așa cum este demonstrat aici, o serie de restricții de natură termotehnologică sau/și termotehnică. În acest articol rolul principal dintr-o serie de restricții este jucat de aptitudinea la clincherizare a amestecului de materii prime și, respectiv, de diferența de bazicitate între oxizi.

Keywords: *clinker composition, optimization, burnability*

1. Introduction

Nowadays industrial processes are subjected to various and, almost in all cases, conflicting constraints. On one hand, product quality, having the outmost importance, should be at its maximum [1-3], while cost-related issues (materials, energy, fuel consumptions etc.) should be at their minimum; overall, plant output is, also, a function of maximum. Even if they were used decades ago, sometimes with success, simple, empirical, techniques to design a process that handles with all these multiple, conflicting objectives are, nowadays, obsolete. Therefore, multicriteria optimization or, at least, scientifically assisted decision-making should be considered at the design of a modern technological workflow.

In the case of the clinkering plant's design, the starting point consists of clinker oxide composition calculation. In cascade, this composition will affect cement properties, raw materials' composition and intake, heat of reaction (and, therefore, fuel intake) etc. Usually, laboratory tests are used to explore the multitude of possibilities as related to, only, clinker quality. As raw materials have various composition from source to source, the clinker composition design stage is mandatory for each cement plant. To explore all options, it is, obviously, an expensive and time-consuming decision. Another possibility is to compute clinker oxide composition by knowing one or more moduli value(s) followed by testing, refining by experiments and finally, validation of the successful composition. Both ones are not accounting for other criteria defining overall processing efficiency, already referred. An alternative to both, is by mathematical programming; this method allows for optimal computation of the oxide clinker composition while also including several constraints. It is of common sense that all calculations should be validated by experiments; the benefit of using computational methods is to reduce the experimental work while incorporating as many constraints as possible.

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In this paper, after a necessary, brief review of the mathematical programming techniques, will follow a series of case studies for clinker oxide composition calculation. The novelty consists of including, along with a series of technological limitations, of several constraints related to raw materials burnability. Raw materials burnability is correlated with heat and fuel consumption, therefore it's evaluation is, also, essential.

2. Theoretical Basis

Simply put, a procedure for acquiring the optimal oxide composition must follow several steps, as suggested in Figure 1.

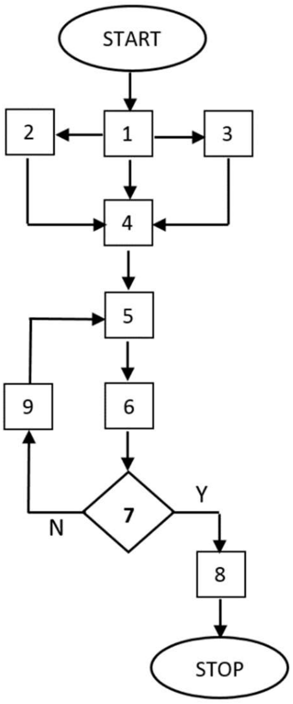

Fig. 1 - Simplified sketch of the optimal clinker oxide composition procedure computation / *Reprezentarea schematică a procedurii de calcul a compoziției oxidice optime a clincherului*

Where steps 1-9 are:
1. Identification of the applicability area of the clinker/*Identificarea zonei de utilitate a clincheului;*
2. Analysis and selection of the existing published data/*Analiza și selecția datelor de literatură;*
3. Experimental data obtained for the specific case/*Obținerea de date experimentale pentru cazul concret;*
4. Selection of the necessary technological constraints/*Alegerea restricțiilor de natură tehnologică;*
5. Selection of the model type followed by the development of the model/*Alegerea tipului de model matematic și implementarea lui;*
6. The analysis of the results/*Analiza rezultatelor;*
7. Decision block/*Bloc de decizie*;
8. Optimal solution of the problem/*Soluția optimă a problemei;*
9. Reevaluation of the Step 5/*Reevaluarea pasului 5.*

2.1. Mathematical model description

Mathematical programming has started world-wide to be used to compute optimal clinker composition after 1970 – and so did in Romania [4].

From case to case, mathematical programing models [5, 6] can be:

- i) deterministic (all variables take a unique value, each); ii) parametric (at least one variable is dependent on a parameter); iii) stochastic (at least one variable takes values given a probability distribution).

- linear and nonlinear (at least one variable is raised to a power different from 1 or at least two independent variables are related by other-than-additive operand.

- with a single or more objective functions.

The rule of thumb is, the more complex the model is, the less accurate can become the optimization result (that may not be unique, in some cases – for example in stochastic modeling). It is possible, though rarely, that complex models can be transformed into simpler ones by using mathematical artifice.

In the specific case of optimal oxide clinker composition, optimization models are deterministic, with a single objective function and either linear or nonlinear.

Mathematical programming models are made of two major blocks: one consists of the model constraints and the other of objective function(s). The most general formulation of a mathematical programing model is, therefore:

$$f_j(x_1, x_2, \dots, x_i, \dots, x_n) \lesseqgtr 0, j = 1..m \quad (1)$$

$$x_i \geq 0, i = 1..n \quad (2)$$

$$(opt)g_k = (min/max)g_k(x_1, x_2, \dots, x_i, \dots, x_n), k = \\ = 1..p \quad (3)$$

If the mathematical model is based on a well-posed problem having an optimal solution and the model is correctly built, it can be solved by using numerical searching methods, SIMPLEX-type algorithms, dedicated software applications. The selection of the solving method is made according to the nature and structure of the model, model's size and difficulty, and accuracy expected from the solutions.

Basically, mathematical programming modeling requires the representation of an *n*-dimensional space of a system of coordination axis $0X_i$, *i=1..n*. Within this space, technological features are described by *m* functions represented by surfaces s_j, $s_j = f(x_1, x_2, \dots, x_i, \dots, x_n)$, *j = 1.. m,* where x_i are optimal values of the independent variables, to be computed. Technological constraints, require, from a geometrical viewpoint, that every surface s_j will split the space in two regions: one that is accepted (when the optimal solution can be reached) and the other which is forbidden. Therefore, a set of constraints such as:

$$s_j(x_1, x_2, \dots, x_i, \dots, x_n) \lesseqgtr 0, j = 1.. m \quad (4)$$

can be drawn.

The system of inequations (4), if it has solutions, describes a *n*-dimensional polyhedral volume $P(x_1, x_2, \dots, x_i, \dots, x_n)$.

The optimization (objective) function is also a surface $S_j(x_1, x_2, \dots, x_i, \dots, x_n)$ that slides parallel to itself, intersecting polyhedral volume $P(x_1, x_2, \dots, x_i, \dots, x_n)$. In the case of the optimal solution, the S function reaches the maximum (or minimum) value, considering the problem's specificity, for a set of values $x_i, i = 1..n$ considered to be the optimal ones for the independent variables.

In the simplest case, the n-dimensional space is represented by a plan, Π (n = 2). The system of coordination axis $OX1/OX2$ is represented in Figure 2:

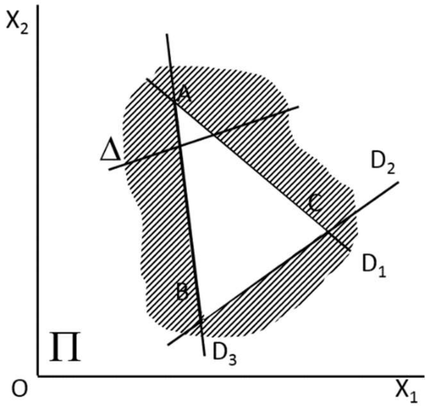

Fig. 2 - Representation of a bi-dimensional search space.
Reprezentarea spațiului bidimensional de căutare.

Technological requirements (model's constraints) are represented, for example, by lines $D_1(x_1, x_2)$, $D_2(x_1, x_2)$, $D_3(x_1, x_2)$, splitting the space Π into two regions. Hatched areas represent forbidden areas, unable of providing solutions. The objective function is modeled by the line Δ; the principle is that, this line slide, parallel to itself to cover the remaining, white area in Fig. 2 made by $D_1 \cup D_2 \cup D_3$ (this white area provides the set of all possible solutions). Per the assumed goal, the objective function represented by the line Δ, can reach the maximum value in the point $A(x_1^0, x_2^0)$ or the minimum value in the point $B(x_1^0, x_2^0)$.

2.2. Identification of the model's parameters

Within the complex area of the cement technology, various combinations that can be made, for example, of the type of mathematical model, and independent variables x_i, $i = 1..n$, constraints f_j, $j = 1..m$, and objective function $g(x_1, x_2, \dots, x_i, \dots, x_n)$ can be formulated.

Independent variables can be chosen from:

- clinker oxide composition: $x_1 = CaO$, $x_2 = SiO_2$, $x_3 = Al_2O_3$, $x_4 = Fe_2O_3$, given as fractions or mass percentages;
- minerals in clinker: $X_1 - C_3S$, $X_2 - C_2S$, $X_3 - C_3A$, $X_4 - C_4AF$ (defined by Bogues Equations);
- moduli composition: x_1 = LSF, $x_2 = M_{Si}$, $x_3 = M_{Al}$, $x_4 = M_H$ etc.

In some mathematical models, constraints can be described by combined independent variables. Generally, constraints can be made of:

- some independent variables that can be bounded or can range due to technological issues;
- clinker properties (described by using the independent variables) such as compressive strength, hydration degree, heat of hydration etc. [6-8]
- indices that can be used to evaluate raw materials burnability such as: heat of reaction Q_r, burnability index *BI,* Refractory Index *IR,* burnability index as given by Humpola, *I,* basicity weight ΔpB, that are given in [9-10].

Objective functions are made of at least one of the properties; the quest is to find composition (independent variables) that provide extreme values (minimum/maximum) for the objective function, as an expression of a technological/economical etc. top requirement.

3. Results and discussions

Relying on the information given in Theoretical Basis Section, there were built a series of mathematical models for computing the optimal oxide clinker composition under various constraints given by raw materials' burnability. Several Case Studies were developed and the resulting models were solved within Mathcad environment.

Case Study #1.
The aim is to compute the oxide composition, x_i, of a clinker for high strength cement application. In the simplest approach, problem constraints (5-9) are made of technological requirements taken from [11]:

$37 \le X_1 \le 56$ (5)

$24 \le X_2 \le 40$ (6)

$0 \le X_3 \le 5$ (7)

$15 \le X_4 \le 19$ (8)

$X_1 + X_2 + X_3 + X_4 = 100$ (9)

and $X_1 - C_3S$, $X_2 - C_2S$, $X_3 - C_3A$, $X_4 - C_4AF$.
The objective function is a property related to the burnability of the raw meal, such as the heat of reaction computed by zur Strassen equation [11], $f_1 = Q_r(X_1, X_2, X_3, X_4)$ or $f_2 = \Delta pB(X_1, X_2, X_3, X_4)$, (10), with ΔpB denotes the basicity weight,:

$$\Delta pB = pB_{CaO} \cdot \%CaO - pB_{SiO_2} \cdot \%SiO_2 - -pB_{Al_2O_3} \cdot \%Al_2O_3 - pB_{Fe_2O_3} \cdot \%Fe_2O_3 \quad (10)$$

pB_{XO} denotes the basicity of the oxide XO.

Function f_1 need to be minimized while f_2 will be maximized. Results are plotted in Figure 3.

For the first case, the heat of reaction Q_r, reached 1795 kJ/kg clinker while the maximum value of the basicity weight was found to be 28.85%. Note that low Q_r and high ΔpB values reflect a better burnability of the raw materials [10]. The analysis of the Figure 3 show somehow close, yet different values of the composition; as a consequence, other criteria should be added and used to obtain the optimal composition.

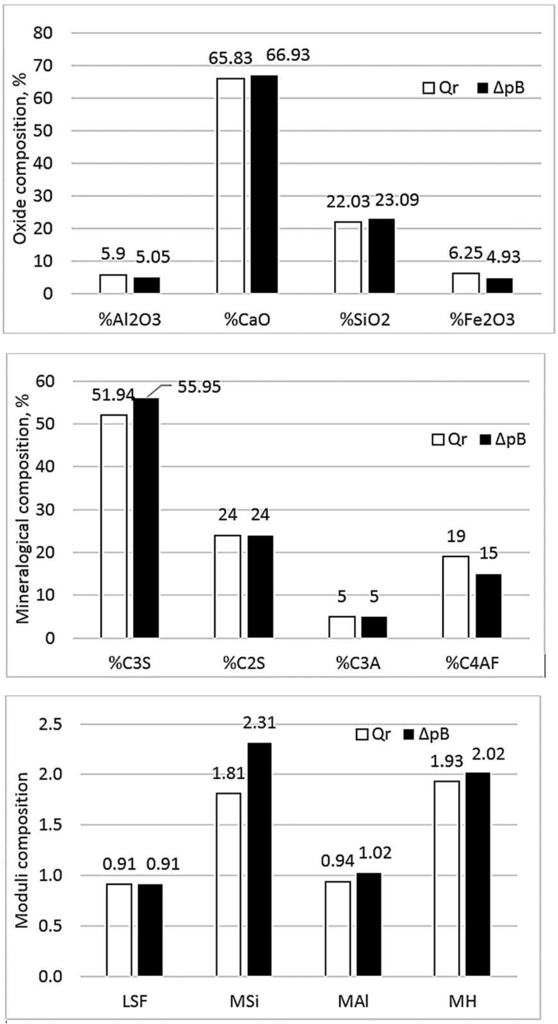

Fig. 3 - Computed optimal clinker composition for the two objective functions (heat of reaction Q_r, respectively ΔpB, the basicity weight) expressed by oxides, minerals and moduli/*Compoziția optimală a clincherului calculată pentru cele doua funcții-obiectiv (căldura de formare Q_r, respectiv ponderea bazicității ΔpB).*

Case Study #2 use other constraints (12-15) taken from [11] for the same type of material as in the previous case study, to obtain extreme (min/max) values of the heat of reaction (3):

$f1 = Q_r = (5.284 \cdot X_1 + 4.641 \cdot X_2 + 6.285 \cdot X_3 +$
$+4.311 \cdot X_4 - 73) \cdot 4.1868$ kJ/kg clinker (11)

subject to:

$62 \leq X_1 \leq 65$ (12)

$5 \leq X_3 \leq 6$ (13)

$X_1 + X_2 + X_3 + X_4 = 100$ (14)

$X_2 \geq 0;\ X_4 \geq 0$ (15)

X_1 – C_3S, X_2 – C_2S, X_3 – C_3A, X_4 – C_4AF, thus resulting in Model M1.

The optimal solution of the model is given in Table 1; for comparison, it was computed the most unfavorable solution, which is given by the objective function:

$(opt) f1 = max\big(Q_r(X_1, X_2, X_3, X_4)\big)$, along with the same constraints.

The result of the maximization reveal that burnability of the raw meal decrease, while the theoretical heat consumption for clinkering increases. Quantitatively, for example, given a clinkering plant with an output of 3000 t/day, the supplementary fuel consumption averages around 7000 t/year.

M2 model can be written with the objective function (16)

$(opt) f = min/max\big(Q_r(X_1, X_2, X_3, X_4)\big)$ (16)

subject to constraints (17-22):

$62 \leq X_1 \leq 65$ (17)

$5 \leq X_3 \leq 6$ (18)

$4X_3 + 4X_4 \geq X_1$ (19)

$2X_3 + 2X_4 \leq X_1$ (20)

$X_1 + X_2 + X_3 + X_4 = 100$ (21)

$X_i \geq 0, i = 1..n$ (22)

Remarks: constraints (19, 20) were obtained by a linear transformation of the double inequation

$2 \leq BI \leq 4$ (23)

that translates to:

$2 \leq \frac{X_1}{X_3 + X_4} \leq 4$ (24)

The optimal value was Q_r = 1774 kJ/kg clinker, 16 kJ/kg clinker higher than the previous minimization model's result. One can be interested in finding the other extreme value, meaning the highest value of the Q_r (a maximization problem). After solving the model, the Q_r resulted in a value of 1804 kJ/kg clinker.

For all cases, various possibilities of expressing clinker composition are given in Table 1.

From a practical viewpoint, the analysis of the Table 1 shows that the results are strongly influenced by the way burnability indices are to be considered. Following the same reasoning thread, it would be interesting to explore what would be the influence of the burnability indices – by providing given values for them – over the heat of reaction.

Case Study #3

In that case study, the model uses the constraints (25-28) regarding mineralogical composition [11], nonnegativity conditions and given (imposed) values of the burnability index $BI \in \{1.5, 2.0, 2.5, 3.0, 3.5\}$ while the sum of all oxides x_i is 100.

Table 1

Results of computing extreme (min/max) values of the heat of reaction

Valorile de extrem (min/max) calculate pentru căldura de formare

Model	%CaO	%SiO$_2$	%Al$_2$O$_3$	%Fe$_2$O$_3$	%C$_3$S	%C$_2$S	%C$_3$A	%C$_4$AF	LSF	M_{Si}	M_{Al}	MH	Min.	Max
	x_1	x_2	x_3	x_4	X_1	X_2	X_3	X_4	y_1	y_2	y_3	y_4	kJ/kg clinker	
M 1	64.16	16.12	8.83	10.89	62.00	0.00	5.00	33.00	1.03	0.82	0.81	1.79	1758	-
M 1	70.67	27.05	2.28	0.00	65.00	29.00	6.00	0.00	0.90	11.86	0.00	2.41	-	1829
M 2	65.49	18.57	7.36	8.58	62.00	7.00	5.00	26.00	0.99	1.16	0.86	1.90	1774	
M 2	68.72	23.46	4.43	3.38	65.00	18.75	6.00	10.25	0.94	3.00	1.31	2.20	-	1804

$37.5 \leq -6.72 \cdot x_1 + 4.07 \cdot x_2 - 7.60 \cdot x_3 - 1.43 \cdot x_4 \leq$
≤ 60 (25)

$15 \leq 5.07 \cdot x_1 - 3.07 \cdot x_2 + 8.60 \cdot x_3 + 1.08 \cdot x_4 \leq$
≤ 37.5 (26)

$7 \leq 2.65 \cdot x_1 - 1.70 \cdot x_4 \leq 15$ (27)

$10 \leq 3.04 \cdot x_4 \leq 18$ (28)

The objective function is given by Eq. (29):

$(min)Q_r = (4.110 \cdot x_1 + 7.646 \cdot x_2 - 5.116 \cdot x_3 -$
$-0.590 \cdot x_4) \cdot 4.1868$ [kJ/kg clinker] (29)

Several correlations with BI can be drawn from the results, such as computed optimal a) mineralogical, b) oxide, c) moduli composition of the clinker (Fig. 4);

Results for the heat of reaction show that:

- if BI can be found in the range 1.5-2.5, the minimal value of the Q_r basically stays constant, i.e. 1678 kJ/kg clinker;
- at values of the BI higher then 2.5, Q_r increases, reaching 1703 kJ/kg clinker for BI = 3 and 1743 kJ/kg clinker for BI = 3.5.

Case Study #4: Relationships between various burnability indices when minimizing heat of reaction, Q_r

This model continues the previous one given in Case Study #3, by adding the equations of percentage of the liquid phase, P_{liq} (30), burnability index, *I* (31), Burnability Factor *BF* (32), Refractory Index *IR* (33), as given by Humpola [9]; these indices are to be computed as well:

$$P_{liq} = 3 \cdot \%Al_2O_3 + 2{,}25 \cdot \%Fe_2O_3 \quad (30)$$

$$I = 0.5 \cdot LSF + 5 \cdot MSi - \frac{20}{MAl} \quad (31)$$

$$BF = \frac{\%C_3S}{\%C_4AF + \%C_3A} \quad (32)$$

$$IR = \frac{\%C_3S + 0.6 \cdot \%C_3A - 0.61 \cdot \%C_4AF}{1.12 \cdot \%C_3A + 1.45 \cdot \%C_4AF} \quad (33)$$

Results are given in Table 2 with the objective function *(opt)f=(min)Q_r*.

Models developed here should be viewed as sub-models of a higher complexity model aiming to design raw materials.

4.Conclusions

Several mathematical programing models were developed based on the heath of reaction and basicity weight as objective functions, to deal with practical issues that can be encountered in modern clinker composition design. Models were built in such a way to incorporate various constraints as an expression of technological and/or thermo-technical industrial demands. Models' complexity has been

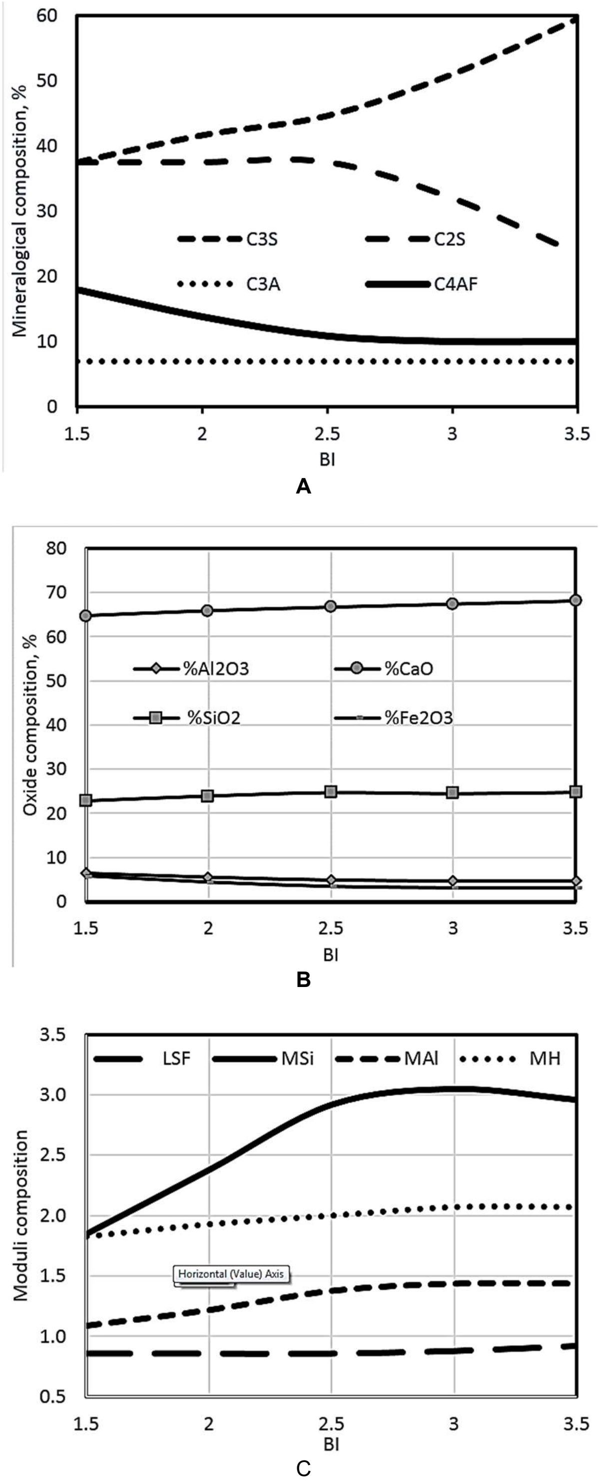

Fig. 4 - Computed optimal a) mineralogical, b) oxide, c) moduli composition of the clinker / *Compoziția optimală calculată a clincherului: a) mineralogică, b) oxidică, c) modulară.*

Table 2

Burnability and burnability-related indices, computed with the objective function *(opt)f=(min)Q_r*.
Indici de aptitudine la ardere, obținuți când se folosește funcția-obiectiv (opt)f=(min)Q_r.

BI	**1.5**	2	**2.5**	3	**3.5**
Pliq	32.64	36.90	22.82	21.66	21.66
BF	104.38	109.81	115.36	118.87	121.37
I	33.80	38.55	43.21	48.20	46.84
IR	0.91	1.34	1.79	2.33	2.58

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gradually increased – that had the effect of closing the boundaries of the search space were the optimal solution can be found. As a consequence, the optimal solution can be found only within the range defined within the search space that provides the properties required for the particular clinker type. As clinkers applications are various, it was proved here that mathematical programing modeling is a useful tool that can minimize the experimental efforts by providing a milestone (a theoretical solution that should be therefore refined and validated by experiments instead of empirical searching through a larger compositional space). Future work will have to test these models – or improved models, that consider other objective functions as well – in an industrial context with a comprehensive approach in mind. Issues such: i) specificity of the clinkering plant (as related to materials, fuels, geometry, process control strategies), ii) accurate measurements of the heat of reaction and of the phases/mineralogical composition according to the real heating curve and iii) accurate mass and thermal balances must be solved.

The novelty of the paper consists in stressing out the influence of the burnability index of the raw meal over heat of reaction optimization. Various other indices, some of them related to burnability, were considered.

Results show clear correlations between all indices and the heat of reaction. It is relevant to observe that clinker heat of reaction represents the major part of the modern clinkering plants' heat consumption (more than 50%). Therefore, heat of reaction minimization has the effect of decreasing overall heat consumption by a proper design of the clinker composition, taking into consideration all necessary indices, according to various industrial requirements. On a more real-world basis, at the industrial level extremely high amounts of fuel consumptions are recorded while pollution being a stringent issue. Economically, it is not *only* the cost related to fuel acquisition that is of interest, but also, in cascade, related to fuel transportation, storage, processing. Therefore even a slight decrease in fuel consumption summed over a larger period of time can help significantly reduce costs and pollution and such mathematical models can be supportive.

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