

THERMO-TECHNICAL IMPLICATIONS OF THE FUEL COMBUSTION WITH SUPPLEMENTARY OXYGEN IN THE CLINKERING PLANTS

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Arderea combustibililor cu oxigen suplimentar sau numai cu oxigen este o metodă relativ simplă de intensificare a arderii. Rezultatul direct este creșterea productivității și scăderea consumului specific de căldură a agregatului termic în care are loc procesul de combustie.

În lucrare se prezintă un model de calcul al procesului de ardere pentru gazul metan folosind amestecuri de aer și oxigen. Sunt evidențiate relații de bilanțuri parțiale cu referire directă la reactanți și la produși de ardere, înăndu-se cont și de reacțiile de disociere.

Se stabilesc: natura și presiunea parțială a componentelor din gazele de ardere, volumul acestora, căldura de disociere și temperatura teoretică. Analiza rezultatelor permite evidențierea procentelor volumetrice de gaze care pot avea efect poluant asupra atmosferei (CO_2 , CO , NO_x).

Fuel combustion with supplementary oxygen or just using oxygen is a relatively simple method of intensifying the burning process. The primary result is the increase of the productivity and the decrease of the specific heat consumption of the thermal installation.

The present paper presents a calculation model for the burning process of the methane gas using mixtures of air and oxygen. Considering the dissociation process, a series of relations of partial balance regarding reactants and combustion products are emphasized.

The nature and partial pressure of hot gases' components, their volumes, dissociation heat and theoretical temperature are established. The analysis of the results emphasizes the volumetric percentages of gases with a pollutant effect upon the environment (CO_2 , CO , NO_x).

Keywords: combustion, supplementary oxygen, heat transfer, specific heat consumption, productivity

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1. Introduction

In the cement industry, fuel combustion provides the necessary burning conditions for the development of the physical-chemical processes of clinker formation.

Regardless of the type of clinkering plant, the heat is produced according to the schema in Fig. 1:

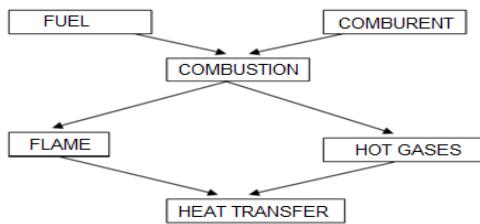


Fig. 1. Combustion process in the rotary kiln

Fuels with high calorific value are burnt in the rotary kiln. For instance natural gas has usually a content of CH_4 higher than 90%.

Usually, in a clinkering plant the comburent used in fuel combustion is air from atmosphere (primary air) and air preheated in the grate cooler (secondary and tertiary air), respectively. At the same time, there is the possibility of using a mixture of air and oxygen in fuel burning. In this case, supplementary oxygen enriches the combustion air in order to intensify the combustion process and increase the thermo-technological performances of the rotary kiln.

Regardless of the type of fuel and nature of the comburent, the combustion process determines the formation of flame and hot gases.

The most important technical parameters of the flame are:

-flame length, that defines the clinkering zone; it is influenced by the nature of fuel and comburent, coefficient of air in excess, burner's characteristics, kiln's diameter, etc;

-maximum temperature and temperature distribution through flame length;
-type of flame (oxidizing/ reducing).

The technical parameters of interest for hot gases are:

-flow;
-temperature;

-chemical composition, including possible polluting gases.

In present article, is presented a mathematical model for the combustion of a gaseous fuel (methane gas) with oxygen-enriched air. The influence of oxygen rate on some characteristics of the hot gases is to be emphasized. At the same time, the results obtained on a rotary kiln are presented as an application.

2. Burning fuels with oxygen-enriched air

The most important thermo-technical parameters for a clinkering plant are specific productivity, specific heat consumption and heat efficiency. The heat transfer in the rotary kiln directly influences these parameters. The hot gases, refractory lining and material perform the complex heat exchange in the rotary kiln, according to the schema in Fig. 2.

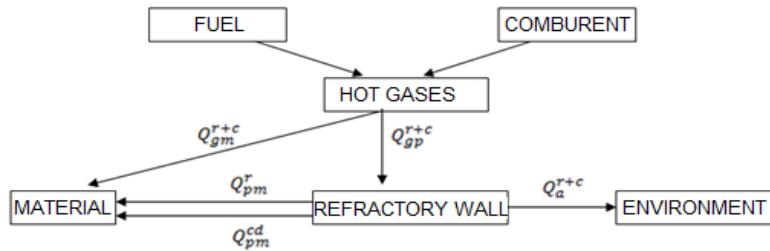


Fig. 2. Heat transfer in the rotary kiln: α – partial coefficient of heat transfer; g – hot gases; p – refractory wall; m – material; r – radiation; c – convection; cd - conduction; a – environment

The heat transfer is mostly (approximately 90%) realized by radiation. The conduction from the refractory lining to material has a less important contribution due to the low value of the heat conduction coefficient (about 2.2 W/m·K).

The emissive power by radiation of the hot gases is mainly determined by their chemical composition and temperature, as well as by the kiln's diameter. [1]

The heat transfer in the rotary kiln may be intensified using several methods:

- the use of high pressure burners;
- preheated combustion air, using heat recovered from the clinker in the grate cooler;
- fuel combustion with oxygen or with oxygen-enriched air.

Intensifying fuel combustion using oxygen-enriched air is a modern method applied in glass industry. In glass melting furnaces, for several types of glass the fuel combustion may be accomplished with 100% oxygen. This method is supported by the improved values of the performance thermo-technological parameters of the plant in comparison with classic combustion. [2, 3]

As the clinkering process requires high temperatures as well, the interest in researching the opportunity of using oxygen-enriched air in fuel combustion in clinkering plants arises.

Present paper emphasizes the implications of fuel combustion using oxygen-enriched air on the characteristics of the hot gases and heat transfer in rotary kiln, as well.

Fuel combustion requires a certain quantity of oxygen, which in classic combustion is supplied by combustion air introduced in the installation. In present

paper the combustion of a gaseous fuel, methane (CH_4), was analyzed. Combustion is accomplished with a mixture of variable flows of air, V_{ar} , and oxygen, V_{O_2} . For gaseous fuels, these flows can be calculated with the following relations [4]:

$$V_{at} = 0.04785 \cdot [0.5 \cdot (\%CO_2) + 0.5 \cdot (\%H_2) + 2 \cdot (\%CH_4) + 1.5 \cdot (\%H_2S) + \sum (m + \frac{n}{4}) \cdot (\%C_m H_n) - (\%O_2)] \quad [\text{Nm}^3/\text{Nm}^3] \quad (1)$$

$$V'_{O_2} = 0.209 \cdot V_{at} \quad [\text{Nm}^3/\text{Nm}^3] \quad (2)$$

where: V_{at} – theoretical volume of combustion air; V'_{O_2} – theoretical volume of oxygen necessary for combustion.

Theoretical volume of air and theoretical volume of oxygen necessary for methane's combustion were calculated with relations (1) and (2), resulting:

$$V_{at} = 9.57 \text{ Nm}^3/\text{Nm}^3$$

$$V'_{O_2} = 2 \text{ Nm}^3/\text{Nm}^3$$

The oxygen percentage in air-oxygen mixture is marked p_{O_2} , and the coefficient of air in excess is marked λ . These parameters are defined by following relations:

$$\rho_{O_2} = \frac{V'_{O_2} + 0.209 \cdot V_{ar}}{V'_{O_2} + V_{ar}} \cdot 100 \quad [\%] \quad (3)$$

$$\lambda = \frac{V'_{O_2} + 0.209 \cdot V_{ar}}{V'_{O_2}} \quad (4)$$

For methane, with respect to p_{O_2} and λ , can be determined the volume of supplementary oxygen, V'_{O_2} and, real volume of air, V_{ar} , respectively,

$$V'_{O_2} = \lambda \cdot V'_{O_2} \cdot (1.264 - \frac{26.42}{\rho_{O_2}}) \quad [\text{Nm}^3/\text{Nm}^3] \quad (5)$$

$$V_{CO_2} = 0.01 \cdot (\%CO_2 + \%CO + \%CH_4 + \sum m \cdot \%C_m H_n) \quad [\text{Nm}^3/\text{Nm}^3] \quad (6)$$

Similar relations can be obtained for other types of fuels, having knowledge of the fuel's chemical composition. [1, 4, 5]

According to relations (5) and (6), the graphs in Figs. 3 and 4 were drawn, representing:

- variation of the supplementary oxygen flow necessary for combustion, with respect to the percentage of oxygen in the comburent mixture for different coefficients of air in excess (Fig. 3);

- variation of the real volume of air necessary for combustion, with respect to the percentage of oxygen in the comburent mixture for different coefficients of air in excess (Fig. 4).

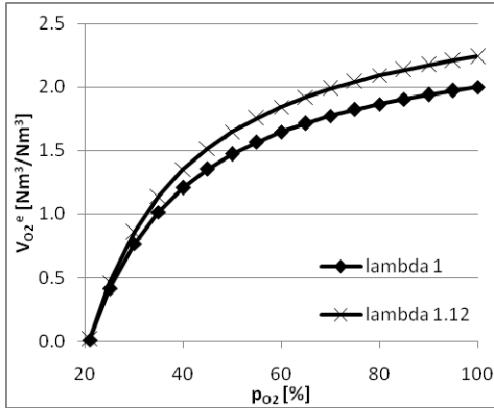


Fig. 3. Variation of the supplementary oxygen flow necessary for combustion, with respect to the percentage of oxygen in the comburent mixture for different coefficients of air in excess

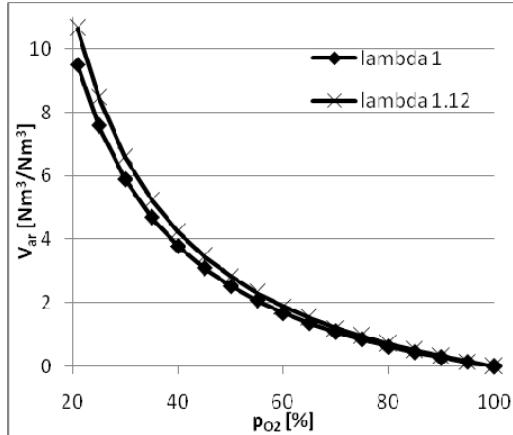


Fig. 4. Variation of the real volume of air necessary for combustion, with respect to the percentage of oxygen in the comburent mixture for different coefficients of air in excess

Fig. 4 shows that the increase of oxygen percentage in the comburent mixture determines the decrease of the real volume of air necessary for combustion. This result is important, because at the same time, the volume of N_2 introduced in the kiln and contained in hot gases decreases. It has a negative effect on the kiln's productivity, diminishing the heat transfer by radiation. Moreover, it increases the heat loss with the hot gases, V_{ga} , exhausted from the plant.

The volume of hot gases resulted from the combustion of CH_4 is calculated with the following relations [4]:

$$V_{ga} = V_{CO_2} + V_{H_2O} + V_{SO_2} + V_{N_2} + V_{O_2} \quad [\text{Nm}^3/\text{Nm}^3] \quad (7)$$

$$V_{CO_2} = 0.01 \cdot (\%CO_2 + \%CO + \%CH_4 + \sum m \cdot \%C_m H_n) \quad [\text{Nm}^3/\text{Nm}^3] \quad (8)$$

$$V_{H_2O} = 0.01 \cdot (\%H_2 + 2 \cdot \%CH_4 + \%H_2S + \%H_2O + \sum \frac{n}{2} \cdot \%C_mH_n) \text{ Nm}^3/\text{Nm}^3] \quad (9)$$

$$V_{SO_2} = 0.01 \cdot \%H_2S \quad [\text{Nm}^3/\text{Nm}^3] \quad (10)$$

$$V_{N_2} = 0.791 \cdot V_{ar} + 0.01 \cdot \%N_2 \quad [\text{Nm}^3/\text{Nm}^3] \quad (11)$$

$$V_{O_2} = 0.209 \cdot (V_{ar} - V_{at}) + V^e_{O_2} \quad [\text{Nm}^3/\text{Nm}^3]$$

$$V_{CO_2} = 1 \text{ Nm}^3/\text{Nm}^3$$

$$V_{H_2O} = 2 \text{ Nm}^3/\text{Nm}^3$$

$$V_{N_2} = 0.791 \cdot V_{ar} \quad [\text{Nm}^3/\text{Nm}^3]$$

$$V_{O_2} = 0.209 \cdot (V_{ar} - 9.57) + V^e_{O_2} \quad [\text{Nm}^3/\text{Nm}^3]$$

$$V_{ga} = 1 + V_{ar} + V^e_{O_2} \quad [\text{Nm}^3/\text{Nm}^3]$$

For the analyzed fuel, CH_4 , in Fig. 5 are presented the values of the volume of hot gases with respect to the percentage of oxygen in the comburent mixture for different coefficients of air in excess.

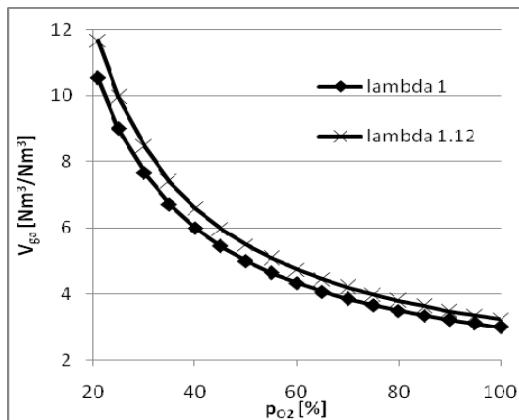


Fig. 5. Variation of the hot gases volume with respect to the percentage of oxygen in the comburent mixture for different coefficients of air in excess

Fig. 5 shows that the increase of the coefficient of air in excess determines the increase of the volume of hot gases, while the increase of the oxygen percentage in the comburent mixture (when $\lambda=\text{constant}$) emphasizes a decrease of the hot gases exhausted from the plant, and therefore the quantity of polluting emissions released in the environment will be smaller [6, 7, 8].

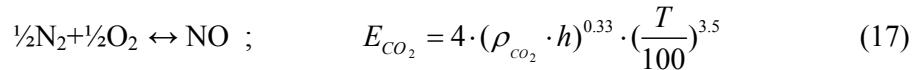
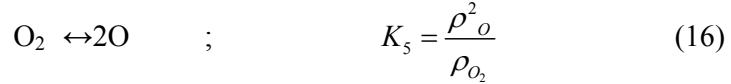
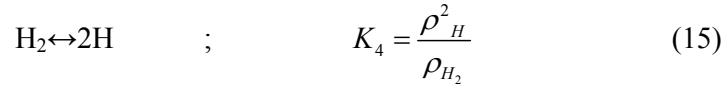
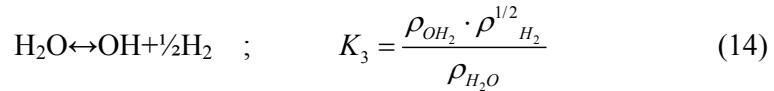
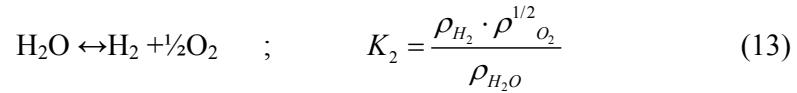
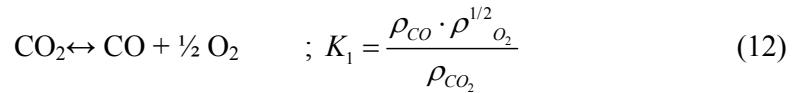
For example, the use of approximately 40% oxygen in the comburent mixture determines a decrease of the volume of hot gases with almost 50% (in comparison with the combustion of CH_4 with air).

During the combustion process, at temperatures above 1000°C, the dissociation processes of certain components of the hot gases are intensified. These processes are influenced by the temperature of the hot gases and pressure inside the kiln, respectively.

3. Dissociation processes in hot gases

Methane's combustion is a complex mechanism, which consists in over 20 reactions, however only for a few of them the reaction rate constants were determined. Thus, the heat released from the combustion of methane cannot be accurately calculated.

The most important reactions, which occur in the combustion of the gaseous fuel CH₄ with air, are:



The dependency between the equilibrium constants, K_i, and temperature is described by this relation [4]:

$$\lg K_i = A_i - \frac{B_i}{T} + C_i \cdot \lg T \quad (18)$$

where: T – temperature [K]; A, B, C – characteristic coefficients for each dissociation reaction.

Reaction constants depend on temperature and, for the reactions presented, their explicit form is of knowledge. A calculation program adapted for the combustion of methane with air and oxygen was used. [1, 4, 5]

The simulations conducted emphasized how p_{O₂} and λ influence the chemical composition and partial pressure of various chemical components (fig. 6-8).

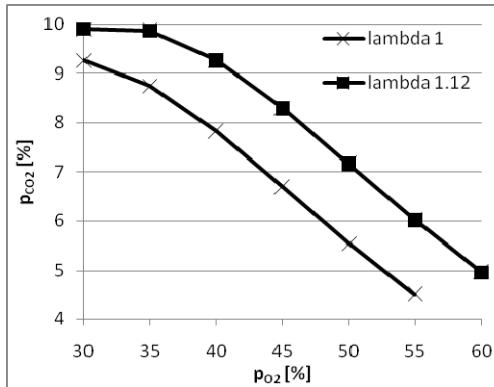


Fig. 6. Variation of the CO_2 partial pressure in hot gases with respect to the percentage of oxygen in the comburent mixture for different coefficients of air in excess

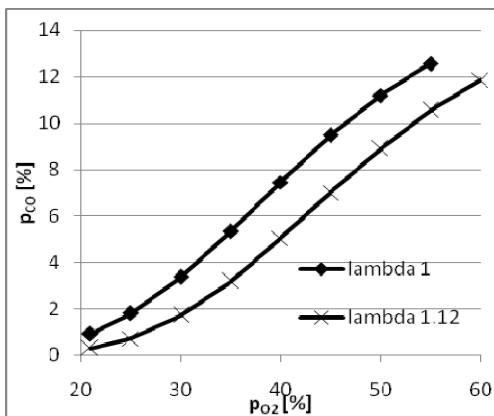


Fig. 7. Variation of the CO partial pressure in hot gases with respect to the percentage of oxygen in the comburent mixture for different coefficients of air in excess

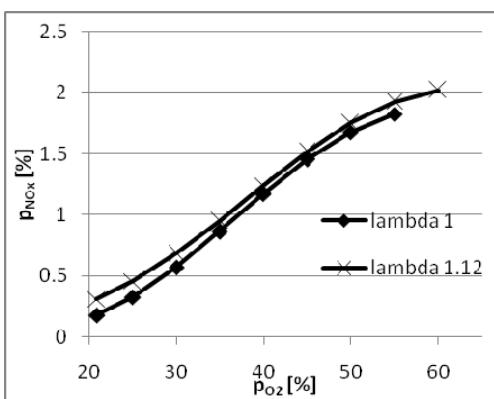


Fig. 8. Variation of the NO_x partial pressure in hot gases with respect to the percentage of oxygen in the comburent mixture for different coefficients of air in excess

Figs. 6-8 emphasize that an increase of the oxygen percentage in the comburent mixture determines a decrease of the CO_2 percentage and an increase of the CO and NO_x percentages in the hot gases. The explanation consists in the fact that the use of oxygen in the comburent mixture determines the increase of the hot gases' temperature, which intensifies the dissociation processes.

The increase of the coefficient of air in excess, λ , determines the decrease of the CO percentage and the increase of CO_2 and NO_x percentages in the hot gases, followed by negative consequences upon the environment.

Figs. 9 and 10 present the relative variations of some components of the hot gases with respect to the percentage of oxygen in the comburent mixture for different coefficients of air in excess ($\lambda=1$ and $\lambda=1.12$).

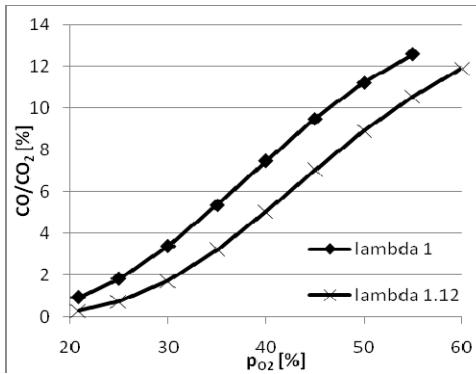


Fig. 9. Variation of the CO volumetric fraction with respect to the percentage of oxygen in the comburent mixture for different coefficients of air in excess

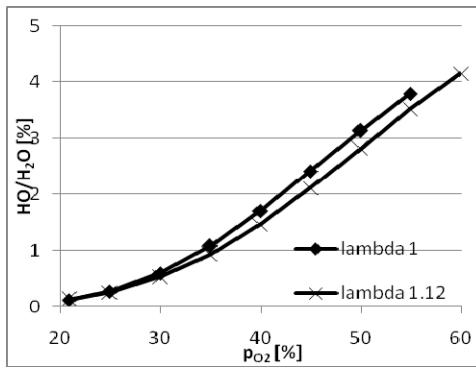


Fig. 10. Variation of the HO volumetric fraction with respect to the percentage of oxygen in the comburent mixture for different coefficients of air in excess

The use of oxygen-enriched air in fuel combustion determines the increase of the theoretical temperature and, therefore, accentuates the dissociation processes. Figs. 9 and 10 show an increase in the percentages of dissociation

products CO and HO in the hot gases, which can be explained by the fact that the increase of the percentage of oxygen in the comburent mixture determines a decrease of the real volume of air and volume of hot gases exhausted from the plant, respectively. At the same time, the temperature of the hot gases increases, favoring the dissociation processes of certain gaseous components.

4. Heat transfer by radiation

In fuel combustion in the clinkering plants, the real temperature of the hot gases or pyrometric temperature, Θ_{ga} , is calculated with the following relation:

$$\Theta_{ga} = \frac{h_i + q_{fiz} - q_{dis} - q_p}{V_{ga} \cdot c_{pgm}} \quad [^\circ C] \quad (19)$$

where: h_i – low calorific value of the fuel; q_{fiz} – physical heat of the fuel and comburent (combustion air); q_{dis} – heat consumed for the partial dissociation reactions of some components of the hot gases; q_p – heat lost outside the kiln (in the environment); V_{ga} – volume of hot gases; c_{pgm} – average specific heat of the hot gases at temperature Θ_{ga} .

If the burning process is considered ideal adiabatic ($q_p=0$), from relation (19) results the theoretical temperature, T_t .

The use of oxygen-enriched air as comburent determines some changes regarding the thermodynamics of the burning process. An important influence is that on the theoretical temperature, due to the decrease of the quantity of hot gases. This is explained by the fact that the use of supplementary oxygen leads to the decrease of the percentage of nitrogen in the comburent mixture. [9, 10, 11]

For methane, the values of the theoretical temperature were calculated considering the percentage of primary air in combustion mixture 10% and 20%, respectively, and the temperature of secondary air 700°C.

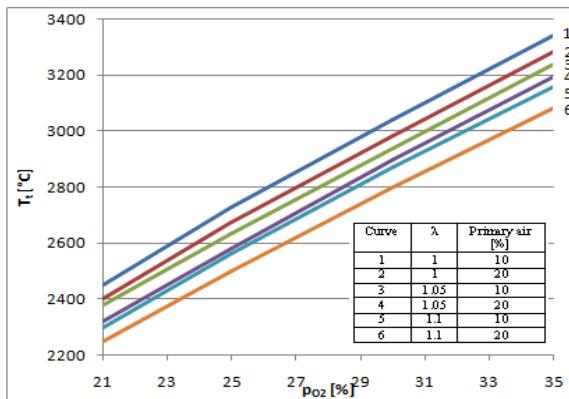


Fig. 11. Variation of the theoretical temperature with respect to the percentage of oxygen in the comburent mixture, coefficient of air in excess and percentage of primary air

Fig. 11 shows that the theoretical temperature increases with the increase of the oxygen percentage in the comburent mixture, whereas the increase of the coefficient of air in excess or the increase of the percentage of primary air determines a slight decrease of the theoretical temperature.

In Fig. 12 is represented the variation of the theoretical temperature with respect to the percentage of oxygen in the comburent mixture, for the coefficient of air in excess $\lambda=1$ and $\lambda=1.12$, respectively.

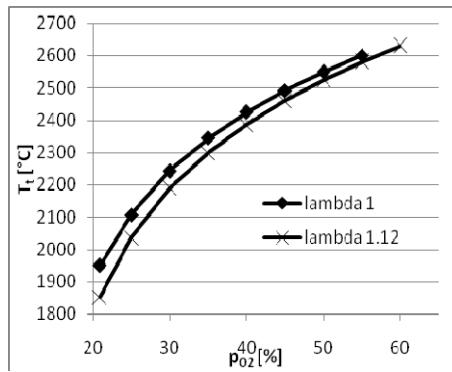


Fig. 12. Variation of the theoretical temperature with respect to the percentage of oxygen in the comburent mixture for different coefficients of air in excess

Fig. 12 emphasizes the increase of the theoretical temperature with the increase of the oxygen percentage in the comburent mixture, while the increase of the coefficient of air in excess determines a slight decrease of the temperature.

In rotary kiln, the heat transfer by radiation is accomplished by heteropolar gases: CO_2 , SO_2 , water vapor, hydrocarbons, CO . Among these gases, the most important are CO_2 and water vapor. The emissive power of CO_2 and H_2O are calculated with the following relations [1, 4]:

$$E_{CO_2} = 4 \cdot (\rho_{CO_2} \cdot h)^{0.33} \cdot \left(\frac{T}{100}\right)^{3.5} \quad [W/m^2] \quad (20)$$

$$E_{H_2O} = 40 \cdot \rho_{H_2O}^{0.8} \cdot h^{0.6} \cdot \left(\frac{T}{100}\right)^3 \quad [W/m^2] \quad (21)$$

where: p_{CO_2} , p_{H_2O} – partial pressure of CO_2 and H_2O , respectively [bar]; h – medium path of the radiation [m] ($h=0.9 \cdot D$, D -interior diameter of the kiln; $h=3.4m$); T – absolute temperature of the hot gases [K].

In order to make a comparison, were considered as reference values the values of the emissive power of CO_2 and H_2O , calculated for $p_{O_2}=0.209$ and $\lambda=1$. The rest of the emissive power values were obtained by varying the combustion conditions (p_{O_2} and λ) and were referred to the reference values. The results are presented in Figs. 13 and 14.

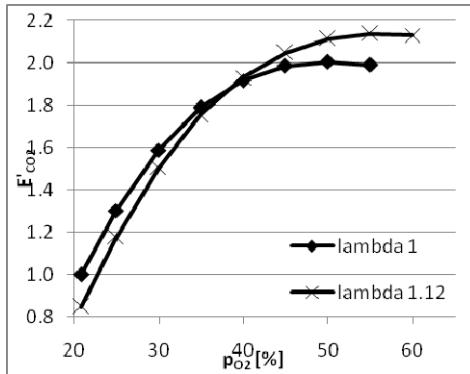


Fig. 13. Emissive power of CO₂ with respect to the percentage of oxygen in the comburent mixture for different coefficients of air in excess

Fig. 13 shows that the emissive power of CO₂ increases with the increase of the percentage of oxygen in the comburent mixture used in fuel combustion, followed by a slight decrease for p_{O₂}>55%. Thus, both for $\lambda=1$ and $\lambda=1.12$, the maximum value of the emissive power of CO₂ is approximately double than the reference value and it is obtained when p_{O₂}=50% and p_{O₂}=55%, respectively.

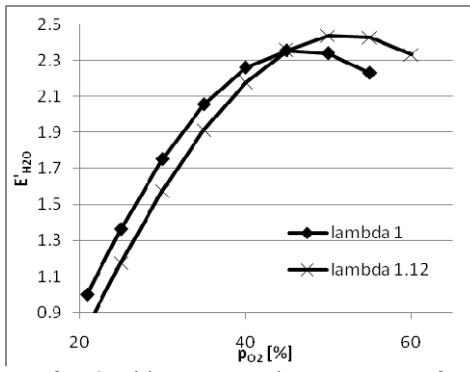


Fig. 14. Emissive power of H₂O with respect to the percentage of oxygen in the comburent mixture for different coefficients of air in excess

Fig. 14 presents the variation of the emissive power of H₂O with respect to p_{O₂} and λ . It shows that, similar to the variation of the emissive power of CO₂, the emissive power of H₂O increases with the increase of the oxygen percentage in the comburent mixture used for combustion. Thus, the value of the emissive power of H₂O when $\lambda=1.12$ and p_{O₂}=50% is approximately 2.5 bigger than the reference value.

5. Implications of the use of oxygen-enriched air in fuel combustion in the clinkering plants

The mixture of oxygen-enriched air used in combustion determines the increase of the theoretical temperature, T_t , which intensifies the heat transfer and, therefore, improves the thermo-technological parameters of the rotary kiln. Thus, the specific heat consumption is diminished, due to the decrease of both the volume and temperature of the hot gases exhausted from the clinkering plant.

In order to emphasize the influence of the oxygen addition to the combustion air, thermal balances were determined for a clinkering plant using the dry process and with the following characteristics:

- fuel: CH_4 ;
- coefficient of air in excess: $\lambda=1.1$;
- cooler's efficiency: $\eta_r=0.70$;
- heat loss in the environment: $q_p=628 \text{ kJ/kg.cl.}$;
- maximum percentage of oxygen in the comburent mixture: 28%.

The results of the simulation are presented in Fig. 15 and in table 1.

Table 1

Thermal balances for the clinkering plant

%O ₂	Supplementary O ₂ Nm ³ /kg.cl.	C _s kJ/kg.cl.
21	-	3210
22	0.009	3172
24	0.024	3118
26	0.036	3068
28	0.047	3030

Considering the thermal balances, the Θ -q diagram was obtained and will be presented in Fig. 15.

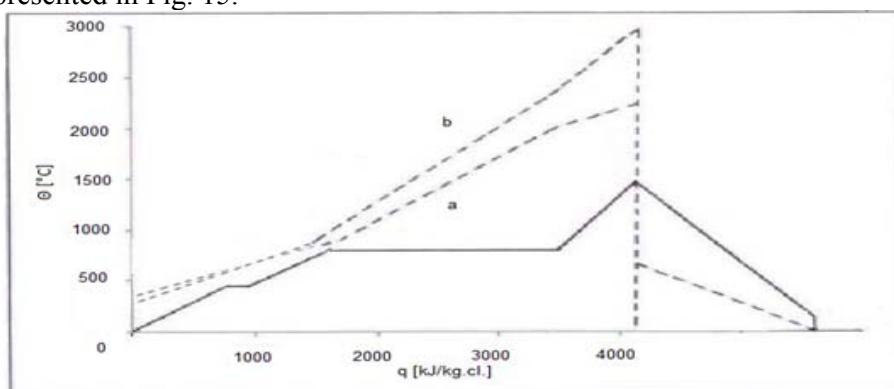


Fig. 15. Θ -q diagram for a clinkering plant using the dry combustion process with: air (a); oxygen-enriched air (b)

Thus, for a clinkering plant using the dry process, the use of 28% oxygen in the comburent mixture determines a decrease of 5.6% in the specific heat consumption, C_s . However, economically, this reduction of fuel implies approximately 9 times higher oxygen consumption. This slight disadvantage can be easily solved by using an oxygen micro-plant near the clinkering plant. This solution is applied frequently in glass-producing plants in Czech, Germany, SUA.

Fuel combustion using oxygen-enriched air has positive influences on the productivity of the clinkering plant, also. The heat transfer is improved by the increase of the hot gases' temperature and, thus, the increase of the difference between gas temperature and material temperature.

The quantity of heat produced per hour and transmitted from gas to material is calculated with the following relation:

$$C_s \cdot P \cdot \frac{10^3}{24} = \alpha_i \cdot S_i \cdot \Delta t_{mi} \quad (22)$$

where: C_s – specific heat consumption; P – productivity per hour; α_i – coefficient of heat transfer; S_i – heat transfer surface; Δt_{mi} – medium logarithmic difference of temperature gas-material.

When using oxygen-enriched air as comburent mixture the relation will become:

$$C_s \cdot P' \cdot \frac{10^3}{24} = \alpha_i \cdot S_i \cdot \Delta t'_{mi} \quad (23)$$

The coefficient of heat transfer (a first approximation) and heat transfer surface are constant in the two situations, however the kiln speed and retention time change in order to maintain the filling degree of the kiln at higher productivities.

The ratio between the hourly productivity of a clinkering plant using oxygen-enriched air in combustion and the hourly productivity of the same plant using classic combustion is calculated with the following relation:

$$\frac{P'}{P} = \frac{\sum \Delta t'_{mi}}{\sum \Delta t_{mi}} \quad (24)$$

The guiding data, which are not detailed in this paper, show that for a clinkering plant using the dry process, a comburent mixture of air enriched with 28% oxygen used in fuel combustion determines an increase of 50% in the hourly production.

Fuel combustion with oxygen-enriched air has a positive impact on clinker quality, by reducing the quantity of alkali in the final product. The explanation consists in the fact that the intense fuel combustion in the kiln determines a high evaporation of the alkalis from the raw meal and, thus, these alkalis are exhausted with the hot gases without interacting with the preheated mixture. This method may be applied when either the raw materials used have a high content of alkali, or the clinker obtained is desired to have a higher quality with a low content of

alkali. This process can be considered for the production of clinkers for white or aluminous cements, when a higher temperature is required in the clinkering zone of the rotary kiln.

The use of oxygen-enriched air in fuel combustion both in glass melting furnaces and in clinkering plants (both rotary kiln and calciner) offers many advantages by improving the performance thermo-technological parameters of the installations. However, the costs implied by this method are not negligible. On one hand, the cost of oxygen is high on the other hand transportation implies supplementary problems.

In this context, a new solution was developed, that of using oxygen micro-plants near industrial plants. Oxygen-producing techniques may vary considering the flow, pressure and purity requirements of each industry. A few oxygen-producing installations for industrial purposes are presented in paper [12].

6. Conclusions

The mixture of oxygen-enriched air used in fuel combustion in the clinkering plants has many advantages, the most important being the increase of the theoretical temperature and decrease of the volume of hot gases exhausted in the atmosphere, respectively.

The positive influence on the theoretical temperature determines the intensification of the heat transfer in the rotary kiln and, therefore, the increase of the productivity and/or decrease of the specific heat consumption, which is equivalent to an economy of superior fuel.

In the present context, that of more and more emphasized crises in the fossil fuel domain, this method is of interest when using alternative fuels with less significant low calorific values to substitute a certain percentage of traditional fuels in the rotary kiln and/or calciner.

The increase of temperature in the burning zone has the disadvantage of intensifying the dissociation processes of certain components of the hot gases. Therefore, the percentages of CO_2 , CO and NO_x in the hot gases increase. However, this effect is balanced by the decrease of the volume of hot gases exhausted from the clinkering plant, which implies a lower quantity (hourly flow) of polluting emissions and, therefore, an alleviation of the phenomenon called greenhouse effect.

Considering both thermo-technological effects and ecological effects, the use of O_2 as comburent in rotary kilns has positive consequences. This method is highly recommended, as the oxygen adduction in the combustion air does not imply special technical problems.

However, the issues regarding the high cost of oxygen, as well as some issues concerning transportation, require a more detailed technical-economical

study. So far, the best solution developed is the use of oxygen micro-plants near industrial plants.

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