INTERNATIONAL JOURNAL OF MULTIDISCIPLINARY RESEARCH AND ANALYSIS

ISSN[Online] : 2643-9875 || ISSN[Print] : 2643-9840

Volume 2 Issue 02 November 2019

Page No.- 28-33

Evaluation of the Alcalis and Sulfur Cycle in Clinker Kilns

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ABSTRACT: In the present work an analysis was made of the formation of crusts or rings in clinker kilns of cement factories in Cuba and Argentina because these formations are one of the most serious problems presented by the kiln areas, which bring with them, stops unnecessary of the entities.

With the use of phenomenological models, general parameters were determined, as well as several residence times of the ovens, as appropriate. In addition, several balances were made in a general way and specifically in several scenarios with the Matlab software in function of the different compounds that enter the furnace or that are formed within it, taking sulfur and sodium as main substances of study, in order , to determine several aspects of them, such as: their influence on the formation of the rings, the quantities present in the system, their main reactions, their behavior in normal operating contexts and in conditions of instability, as well as possible solutions for its mitigation and control in kilns.

The calculations showed that sulfur and sodium should be managed close to the parameters established by the entities for a good operation of the ovens, thus avoiding unnecessary stops due to ring formation.

Keywords: Ring; Sulfur; Kiln; Matlab; Reactions

1. Introduction

In the cement factories unnecessary stops occur due to problems in the oven. One of the main problems is the formation of rings within the equipment, mainly sulfur, alkali or clinker, which directly influence the operation of the furnace and the quality parameters of the final product of this stage.

Raw materials provide different compounds such as calcium oxide, silica, iron and other minority compounds, Moreira (2011). All these elements make up the flour which enters the oven once prepared, within the equipment chemical reactions occur that give way to the formation of the main mineralogical components of the clinker (final product that is obtained from the cooking of the flour), (Canales et al., 2004) However, there are reactions that give way to minority compounds that may or may not leave together with the clinker, being part of it in smaller numbers. Among the oxides involved in these reactions are sodium and potassium (alkalis), which have a high selectivity to react with sulfur (SO_3) within the system, sometimes raw materials lack alkalis and are rich in sulfur trioxide, or vice versa.

Therefore, the main objective is to evaluate the process of ring formation in clinker ovens.

2. Methodology

The following aspects were taken into account for the development of the balances.

- Two cement factories were taken as a reference: A dry process industry in Cuba and a wet process entity in Argentina, with the aim of validating the model proposed for carrying out balances under different conditions.
- The balances focused mainly on Sulfur Trioxide and Sodium Oxide.

2.1 Model selection

The rotary kiln responds to the model of a continuous piston flow reactor. The main characteristic of this type of reactor is the change of the conversion according to the position of the reactants within the equipment.

Therefore, the operating model that was selected was that of mixtures of particles of different sizes, but constant, piston flow of solids and gas of uniform composition, Levenspiel (1987).

This model was selected because it is a heterogeneous reactor, with solid-solid and solid-fluid reactions and there is also a feeding of solids of different sizes. Based on the unreacted core model

2.2 Balances of the model under study.

To study the processes of ring formation in the oven, a model was taken and balances were made, in order to evaluate the scenarios.

Oven in Cuba

- First scenario: The oven working in conditions of high sulfur (0.63%) and low value of sodium oxide (0.15%).
- Second scenario: The furnace working with an addition of the sulfur inhibitor additive under high sulfur conditions.

Furnace in Argentina

- Third scenario: The oven working in conditions of high sodium (0.60%) and high sulfur values (0.97%).
- Fourth scenario: The furnace working with hundreds of sulfur in the conditions of the third scenario.

In addition, common parameters were determined for the scenarios, such as the movement of solids and residence times, the calculations in each of them were resolved using Matlab software.

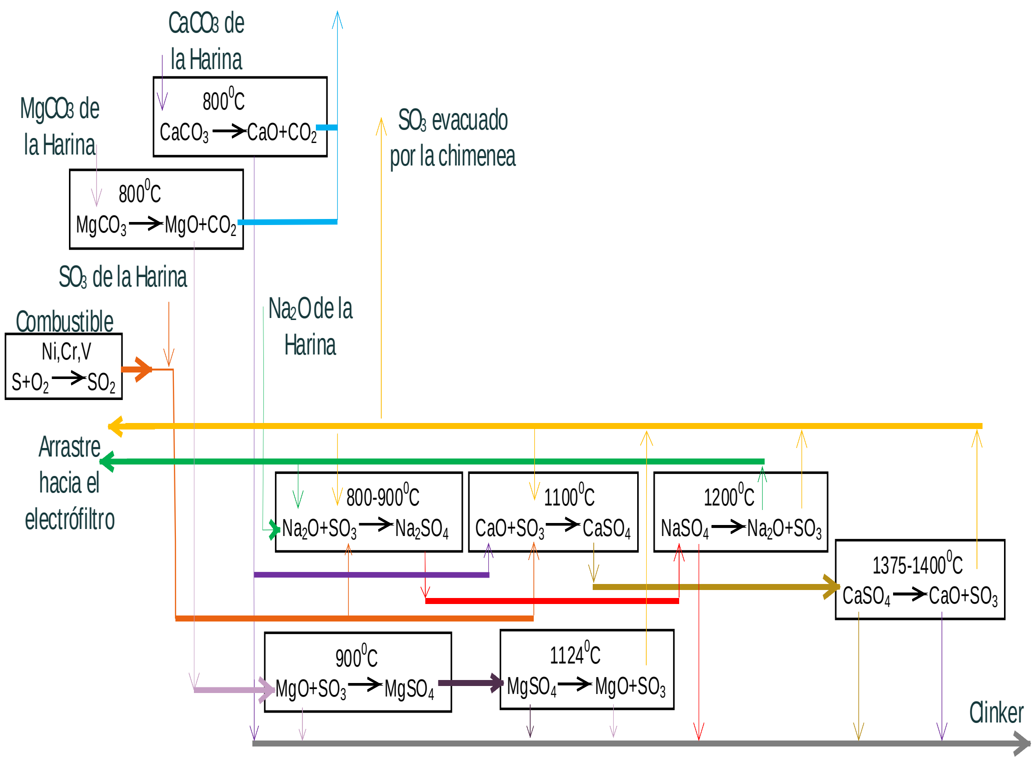

Figure. 2.1 Outline of the model of the reactions of the furnace of Cuba (own elaboration).

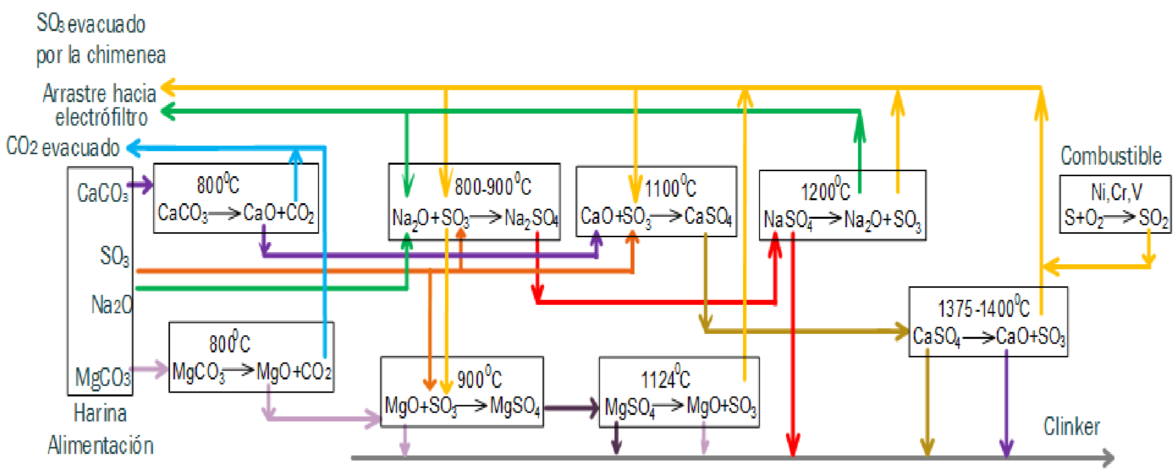

Figure. 2.2 Outline of the model of the oven reactions in Argentina (own elaboration).

3. Results and Discussion

Table 3.1 shows the results of the corresponding Froude number for each oven

Froude Number	Value	Movement type
Fr oven from Cuba	0.033	Rolling
Fr oven from Argentina	0.0037	Rolling

3.1 Results of the Furnace of Cuba Evaluation.

3.1.1 First scenario

Once the equations to be used to calculate the residence time (Tt), the depth profile (As) and the solid material flow rate (qs) are calculated, the calculations are carried out in the Matlab software, obtaining the results shown then.

Table. 3.2 Results of the parameters of the furnace of Cuba

Equation	Data	Unknown	Result
$Tr_2 = \frac{1{,}77 * L * \sqrt{\theta}}{\beta D_{Hi} w} * \frac{\frac{D_{Hi1}}{D_{Hi}o} - (0{,}8 - 0{,}3 * \frac{L}{D_{Hi}})}{0{,}3 * \frac{L}{DHi} + 0{,}195}$	DHi1= 11,48 feet DHio= 8,85 feet L= 141 feet	Tr2	17 min
$\frac{dr_o}{dx} = \frac{3q\sin(\theta)}{4\pi w(R_{Hi}^2 - {R_o}^2)^{3/2}\cos(\theta)} - \frac{\beta}{\cos(\theta)}$	β = 2,5 degrees θ = 36 degrees	ψ	10,94 degrees
$dAs = 2R_{Hi}\sin^{-1}\left(\frac{({R_{Hi}}^2 - Ro^2)^{\frac{1}{2}}}{R_{Hi}}\right)dR_{Hi}$	RHi= 1,75 m Ro= 1,35 m	As	0,40 m2
$qs = \frac{4\pi w}{3}\left(\frac{\beta + \psi\cos(\theta)}{\sin(\theta)}\right)(R_{Hi}^2 - {R_o}^2)^{3/2}$	RHi= 1,75 m Ro= 1,35 m	qs	405.67 m3/h
$Tr_3 = \frac{L * As}{qs}$	L= 88.56 feet	Tr3	17 min
Tt=Tr2+Tr3	Tr2=17 min Tr3=17 min	Tt	34 min

These results corroborate what was stated by Saeman, WC (1951) and D. Sullivan, J, (1927), the residence time will be more affected if the restriction is close to the exit of the oven, as can be seen when compare the residence time the team has by design (30 min) with hours would be approximately 7.68 tons, which is a dangerous value for oven operation.

3.1.2 Second scenario

The use of sulfur inhibitor additives has demonstrated viability in the treatment of high percent of this compound in the oven.

Tabla 3.3 Balance results for the first scenario

SO3 in the system	Values	Unity
SO3 system input	31,14	kmol
SO3 evacuated in the clinker	23,68	kmol
SO3 evacuated by chimney	0,20	kmol
SO3 other reactions	3.258	kmol
SO3 remaining or retained	4,00	kmol

The first stage (34 min) shows an increase of only 4 min. Subsequently proceed to These additives are introduced to the process mixed with the petcoke at a rate of one liter per tonne of fuel. solve in the Matlab the balances of the sulfur cycle of the first scenario.

The value obtained from remaining or retained SO3 indicates that the system is retaining sulfur, as you can see the retention obtained (taking the data from Table 3.5 on the basis of one hour) turned out to be 4.00 kmol, this being 320 kilograms . In 24 The residence time for this scenario is equal to 34 min, corresponding to the value of the first scenario, since the solution starts from it with the same conditions and other equal parameters.

The inhibitory additives will act on the catalysts of the reaction of formation of SO3 (chromium, nickel and vanadium mainly) leaving balanced the amounts of sulfur with other substances (mainly alkalis) so that they are the ones in charge of finishing evacuating this element from the oven.

Once the calculations were made in the Matlab software, the results shown below were reached.

As can be seen, there is no remaining or retained SO3, due in large part to the action of the inhibitory additive. The sulfur captured by the additive is evacuated from the system mainly in the clinker and the rest goes out through the chimney.

3.2 Results of the oven evaluation of Argentina.

3.2.1 Third scenario

The clinker production process of the cement factory in Argentina is carried out by means of the wet track in a 90 meter long oven, it is divided into several areas where the diameter of the equipment varies.

The residence time (Tr) for the section containing the handover and sintering zones was calculated by the equation proposed by Saeman W. C (1951).

Table 3.4 Balance results for the second scenario.

SO3 in the system	Values	Unity
SO3 system input	31,14	kmol
SO3 evacuated in the clinker	17,91	kmol
SO3 evacuated by chimney	0,16	kmol
SO3 other reactions	3,258	kmol
SO3 inhibited by Aditek	9.8	kmol
SO3 remaining or retained	0,00	kmol

Table 3.5 Results of the parameters of the oven in Argentina.

Equation	Data	Incognito	Result
$dAs = 2R_{Hi}\sin^{-1}\left(\frac{({R_{Hi}}^2 - Ro^2)^{\frac{1}{2}}}{R_{Hi}}\right)dR_{Hi}$	RHi= 1,3 m Ro= 1,05 m	As	0,26 m^2
$qs = \frac{4\pi w}{3}\left(\frac{\beta + \psi\cos(\theta)}{\sin(\theta)}\right)(R_{Hi}^2 - {R_o}^2)^{3/2}$	Ψ=0	qs	0.31 m^3/min
$Tr = \frac{L{*}As}{qs}$	L= 32 m	Tr	27 min

As you can see the residence time of these areas of the oven is 27 min, which coincides with that proposed by D. Sullivan, J. (1927) for an oven that has the characteristics outlined above, the value of residence time It will be referenced for the other calculations.

Subsequently, the sulfur cycle balances of the third scenario are resolved in the Matlab.

The value obtained from the remaining or retained Na2O indicates that the system presents alkaline evacuation problems, as observed retention can be observed (taking the data from Table 3.14 on the basis of one hour) turned out to be 0.66 kmol being 79.03 kilograms For approximately 24 hours it would be approximately 1.90 tons, which is a danger value since with this retention of Na2O in the system if measures are not taken to counteract or reduce these conditions the formed ring can affect the operation of the furnace.

Table 3.6 Results of the balances as a function of sulfur.

SO3 in the system	Values	Unity
SO3 system input	2,33	kmol
SO3 evacuated in the clinker	2,18	kmol
SO3 evacuated by chimney	0,06	kmol
SO3 other reactions	0,13	kmol
SO3 remaining or retained	0,00	kmol

As can be seen in these conditions, there is no remaining or retained SO3 in the system that is one of the main ring-forming compounds in clinker ovens, however, when analyzing the alkalis (in this case sodium), they are obtained The following results.

3.2.2 Fourth scenario

The residence time for this scenario is equal to 27 min, corresponding to the value of the third scenario, since the solution starts from it with the same conditions and other equal parameters.

As noted above there is an imbalance between sulfur and alkalis of the system, so it is done.

Table 3.7 Results of the balances according to the Sodium.

Na2O in the system	Values	Unity
Na2O system input	3,02	kmol
Na2O evacuated in the clinker	2,24	kmol
Na2O other reactions	0,13	kmol
Na2O remaining or retained	0,66	kmol

it is necessary to find the optimum SO3 percentage to achieve the evacuation of the sodium retained in the oven, for this purpose a percentage of sulfur greater in the raw materials of 1.29% is taken as a starting point and the mass balances are carried out in the Matlab software obtaining the results shown below.

2. With the phenomenological models developed to characterize and evaluate the dynamics of fluids within clinker furnaces, it was determined that the movement of solids is of the rolling type, which coincides with the models proposed in the literature for a team of this type.

Table 3.8 Results of the balances for the fourth scenario.

Na_2O in the system	Values	Unity
Na2O system input	3,02	kmol
Na2O evacuated in the clinker	2,94	kmol
Na2O other reactions	0,13	kmol
Na2O remaining or retained	0,00	kmol

As can be seen, there is no remaining or retained Na2O, due in large part to the action of the sulfur increase in the system, which was 0.32%. To achieve the increase of sulfur in the raw materials it is necessary to carry out an in-depth study of the quarries and subsequently evaluate the addition of another raw material by performing the corresponding mixture calculation.

3. Using a program in Matlab, the alkali-sulfur cycle in the furnaces was simulated, which allowed identifying and evaluating the main components of this cycle.

4. The results obtained from the modeling and simulation in Matlab software showed that the evaluation of the alkali-sulfur cycle through the balances of chemical reactions in the proposed schemes is feasible.

4. Conclusions

1. The diagnosis made in the clinker production process of the cement factory in Cuba, evidenced that there is sulfur retention in the oven which causes the formation of rings, and in the case of the factory in Argentina it was shown that rings are due to sodium retention in the system, both they bring process interruptions.

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