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Thermoviscosity mechanism approach in forming fayalite-type ceramic accumulations in particle separators in CFD reactors

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Abstract. - This article presents the fundamental bases to generate knowledge in forming fayalite-type adhesions. Likewise, to determine the conditions that favor the change of viscosity and consequent conditions of the plasticity of the studied system. The analysis focuses on temperatures between 723K and 1023K and pressures above 5 bar. As a result, the formation of adhesions observed in the production process that contain the materials involved and commonly associated with the collision between the particles are estimated, as well as the effect of the different associated energies that arise from this phenomenon. This mechanism may apply to the study of the adhesions of other ceramic materials under thermoplastic conditions with behavior in similar conditions to the studied ceramic system, using the equation modified to that proposed by Mc Lean for thermoelasticity of metals.

Keywords: Thermo-plasticity, relative viscosity, wustite, particle collision, sticking, creep, fayalite.

Enfoque del mecanismo de termoviscosidad en la formación de acumulaciones cerámicas de tipo fayalita en separadores de partículas en reactores CFD

Resumen: Este artículo presenta las bases fundamentales para generar conocimientos en la formación de las adherencias de tipo fayalita. Así mismo, para determinar las condiciones que favorecen el cambio de viscosidad y condiciones consecuentes de la plasticidad del sistema estudiado. El análisis se enfoca en los rangos de temperaturas entre 723K y 1023 K y presiones superiores a 5 bar. Como resultado, se estiman las formaciones de las adherencias observadas en proceso productivos que, contienen los materiales involucrados, y asociadas comúnmente al choque entre las partículas, así como el efecto de las diferentes energías asociadas que se desprenden de este fenómeno. Este mecanismo puede ser aplicable al estudio de las adherencias de otros materiales cerámicos en condiciones termoplásticas con comportamiento similar en condiciones al sistema cerámico estudiado, utilizando la ecuación modificada a la propuesta por Mc Lean para termoelasticidad de metales.

Palabras clave: Termo plasticidad, viscosidad relativa, wustita, choque de partículas, pegado, fluencia, fayalita.

I. INTRODUCTION

These processes tend to operate intermittently during the different iron ore manufacturing processes in which the Prada [1] fluidized bed technology is used for processing. In these processes, de-fluidization is generated, which is caused by the adhesion of partially reduced iron in the fluidized bed D. Fuller [2]. This defluidization is also associated with the formation of accretions on the internal metallic surfaces of cyclones, caused by the collision between the particles at temperatures below the melting point of iron, causing intermittent operation. In this work, the concept of interaction between particles is associated with the apparent viscosity phenomenon. Zhang et al. [3] proposed quantitatively expressing iron-containing particles to resist creep movement in plasticity. It has also been cited that this concept includes the resulting combination of external friction interactions. These cohesive forces include the Van der Waals force, interfacial attraction, and liquid-solid bridges, which are not yet considered to describe particle agglomerations in fluidized bed processes.

That said, the thermo-viscosity approach to the mechanism of formation of adhesions of silicates in a particle separator offers the possibility of explaining the model in terms of the condition that favors a change in viscosity, the consequent condition of plasticity and flow of the resulting materials to form the observed adhesions that contain the involved materials and that are generated. This is based on the release of energy from the particle collision and impact on the interior surface of the particle separator, as well as the resulting temperature that favors the conditions described above. At this point, it is worth an approach to rheology, as the branch of physics deals with the deformation and flow of solid and liquid materials but also applies to complex microstructures, such as silicates.

To study the materials above, those whose viscosity changes with the deformation rate in a specific temperature range are considered and are called non-Newtonian fluids. Therefore, to deal with this apparent discrepancy, it has been accepted that rheology, in general, might be the answer because it accounts for the study of liquids with viscosity dependent on the deformation rate. Its theoretical aspects are the relationship of the flow behavior for the deformation of the material and its internal structure, such as silicates, and the behavior of this type of material that cannot be described by classical fluid mechanics or elasticity.

II. THE PROPOSED MECHANISM

The phenomenon studied is located inside a particle separator inside fluidized bed reactors during the reaction of ferrous oxide to metallic iron, in the range of 500 °C to 800 °C and pressures higher than 5 bar. The adhesions that the reacting materials contain are involved, mainly FeO and SiO2, and are generated as a product of the impact of the particles and the associated energies released at temperatures under the operating conditions described above.

The proposed mechanism aims to consider the condition of the rotating particles within the particle separator. Therefore, the mechanism is based on mathematical formulations to express the phenomena considered in terms of apparent viscosity and consequent plasticity observed in samples of the adhesions of materials with a high presence of ferrous oxide collected from industrial processes. These adhesions were analyzed using Bauman print-type macro etch techniques to observe distribution lines of non-metallic materials and particle flow lines. This provided vital information to understand the proposed mechanism explaining adhesion formation within the particle separator. The formation of adhesions is based on the condition that favors a change in the apparent viscosity and, consequently, the appearance of the condition of plasticity and fluidity of the resulting materials to form the observed samples. The proposed mechanism is schematically described in Fig. 1.

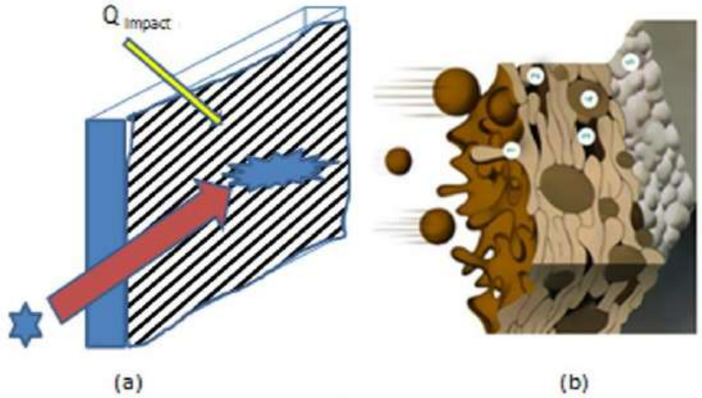


Fig 1. (a) Represents the pattern of impact of a particle against a metal wall (b) Indicates how the layers of the crust are formed by thermo adherence.

In this mechanism, the solid particles heat up during the reaction conversion of ferrous iron to metallic iron. When they impact the surface of the steel and its roughness, they become viscous as a consequence of the impact, it releases enough energy Fig. 1a, and it becomes a material viscous (1), which crawls impelled with the gas flow superimposing the previous imperfections (2) and creating pores (3) and generating the silicates of Fayalite Fig. 1b. Port analogy is a process similar to that of surface thermoactivity.

A. Energy balance

The energy balance was calculated and presented in a previous document by Echegaray [4] and is summarized in Table 1.

Table 1. Energy balance within the particle separator.

Symbol	Energy	(KJ/mol)	(Kcal/mol)
Ec	Impact on cyclone wall	103	30
Ev	FeO vacancies energy	474	113
Ep	Particle's impact	13	3
Ei	Inelastic collision	70	17
Total	Total	660	163

The calculation of the total energy agrees with the reported energies of Gaskell [5] for the Fayalite formation reaction, as well as with the softening point of silica in the range of 2000 ° C of approximately 599 KJ reported by Ringdalen [6] With the total energy calculated of 660 KJ/mol, which exceeds the softening of silica, it is possible to conclude that the formation of Fayalite in the temperature range studied is thermodynamically possible during an intermediate viscous condition.

B. Effect of temperature on apparent viscosity

According to the previous calculations, the total energy balance is 61 KJ/mol over the 599 KJ/mol for the softening of the SiO2 particle formation of the Fayalite silicate, notably coinciding with the range of 61 to 65 KJ/mol considered as compensated activation energy for the deformation-creep of the silicate particles to occur.

To obtain the effect of temperature on apparent viscosity, it is necessary to accept the past energy condition of the solid particles in the gas-solids mixture. These particles that travel in the hot gas stream not only have a suitable thermal condition but, on the one hand, the iron-containing particles are in a transient structure from ferrous oxide (FeO) to iron, which in turn means an additional energy gradient associated with vacancies, which release said energy. On the other hand, among silica particles in a collision path with wustite, these particles are found in conditions of energy levels similar to thermal coating particles projected onto a metal surface at high speeds. With these conditions, the occurrence of the fusion reaction between particles is assured.

C. Adhesions of silicate by action of fluence

Having assumed the formation of a viscous phase formed by FeO-SiO2 as essential components for the formation of silicates, together with the additional presence of MgO and metallic iron, it is possible to assume that the viscous phase was formed under a gas velocity of 75m/s entering each cyclone at that time, the appearance of a deformation force will create a thermo-viscosity situation. The presence of the deformation force on the viscous silicate led to the consideration of a combination with a creep regime.

Considering the creep regime, a dependent temperature effect, it is necessary to consider the melting temperature (Tm) of the species involved. In this case, the species in question is metallic iron. This relationship was driven by the different flow rates for metal powders, covering roughly the metal temperature ranges from 0 to 1 times Tm. This range has a lower range of 0.3-0.5 of the melting temperatures of the metal considered, for which it was defined as a creep dependent on the logarithmically of the temperature, which is governed by an Arrhenius factor, similar to liquid metal streams. The temperature and tensile creep stress dependence have been studied in α-ferromagnetic iron in the temperature range 620 °C -700 °C.

The activation energies for creep can be made using the slope change method. In this way, it is shown that the activation energy compensated by the mathematical simulation model is essentially independent of the initial stress and of the deformation up to the solidification point. With this method of slope change, an activation energy compensated by the model of 65 kcal/mol is obtained. On the other hand, when graphing the logarithm of the variation of the deformation paid by the model versus the inverse of the absolute temperature, it allows to obtain a straight line that represents an activation energy compensated by the model of 62 kcal/mol, K Murty et al. [7]. These values are essentially by the self-diffusion value in this temperature range.

D. Thermoplasticity and fluence relationship

The activation energies, both the creep and the self-diffusion, indicate that the creep process mechanism is controlled by diffusion and, therefore, by a non-conservative dislocation movement. This means that at the speeds of deformation and temperatures used, the average vacancy concentration is only a slight disturbance of the equilibrium vacancy concentration in the tested undeformed samples. The creep data available on some FCC metals shows that obtaining a reasonable energy estimate for the movement of vacancies is possible. From a thermo-mechanical approach, in this work, it was possible to establish the physical meaning of the energy released by a defined particle size within the separated particle. Chica et al. [8] explain that it starts from Cauchy's first law and multiplies both sides by the viscosity (v). Rearranging the terms, we finally get that:

$$\frac{D}{D_t}\left(\frac{v^2}{2}+\varphi\right)=(\nabla.T).v+T:\nabla v \qquad (1)$$

The product $\nabla \boldsymbol{v}$ represents viscous dissipation Ev. The formation of accretions in the form of shells in the cylindrical zone in the temperature range above 600 °C and pressures above 10 bar is possible in fluidized bed processes when working with molecular weights in the gas of 10 gr/mol. Therefore, the appearance of thermoplasticity in the studied temperature range 600 °C (873K) to reach the melting point of iron requires validation since, from the point of view of the collision between particles, enough energy may be released to go to the point of thermoplasticity, that is, it starts the process of softening the particles.

E. Effect of temperature on apparent viscosity

Once the apparent viscosity of the studied components has been identified and quantified, as well as the participation of creep in the proposed mechanism, the next step is to determine the effect of the critical temperature on the occurrence of thermoplasticity. As mentioned above, in the mechanism studied, there is an initial conditioning of the partially reduced iron oxide due to its heating by the gas flow. This precondition has been related to the adherence tendency of the minerals used in fluidized bed reduction processes. This is a particular tendency of the different minerals and their mixtures used in the process. In Fig. 2, the transition of the formation of the metallic iron step is shown. This figure shows the effect of the formation rate of metallic iron, opposite to the reduction of ferrous iron, on the critical adhesion temperature during the passage from wustite to iron. Depending on the reduction stage, hot particles naturally develop an active sticking tendency or sticking potential.

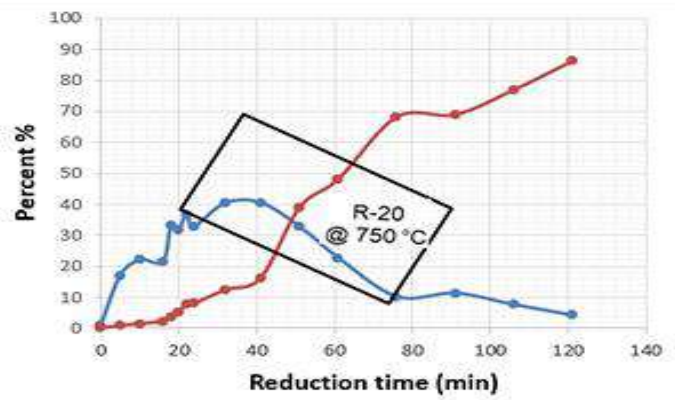


Fig 2. Transformation of ferrous iron into metallic iron in the studied area.

The data for the elaboration of Fig. Three were obtained from industrial tests used in a C F. D plant using mixed Venezuelan and Australian mineral mixtures that are 100 percent Australian. From this figure, it is possible to estimate the ranges of the temperature values for the occurrence of sticking of iron particles, partially metalized as a function of the formation of metallic iron of the particles during their transfer into the particle separators. The temperatures obtained can be assumed as actual, working, or operating temperatures. This temperature creates an activated state of the particles, prone them to the appearance of different stages of the sticking phenomena, such as bogging or particle agglomerations in the fluidized bed, crustal adherences in the upper cylindrical section of the particle separator sand sintering in the returning particles in the separator leg in the lower portion.

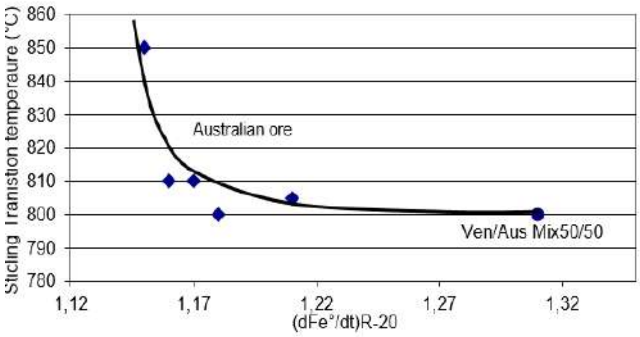


Fig 3. Effect of the metallization rate on the critical adhesion temperature.

This activated adhesion potential, thus developed by the partially reduced iron oxide particle, enters the particle separator on the path of eventual collision with the clean steel surface during initial accretion formation or further accretion development. This kinetic behavior can be expressed mathematically according to the following equation,

$$(T)\ \text{real operation} = 3.987,\ (dFe^{\circ}/dt)2\ -9.974,9\ (dFe^{\circ}/dt) + 7027,8 \qquad (2)$$

With a correlation R^2 of 0,7684, representing the reliability of industrial data more significant than 85%, it is considered very acceptable because it is industrial data.

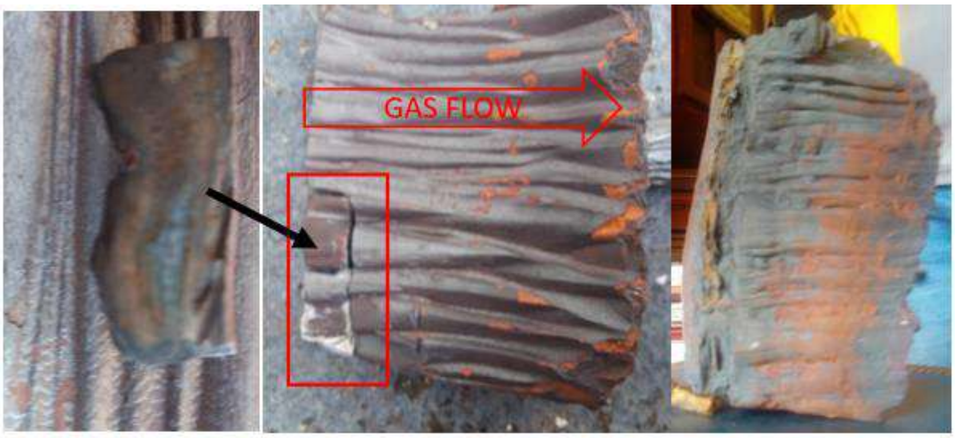
III. METHODOLOGY

At this point, the appropriate theoretical and thermodynamic basis for the proposed mechanism has been established, and the empirical relationships between the critical temperature variables of adherence, viscosity, and creep of the silicates formed during the collision of solid particles as well as with the impact that exists between the particles and the surfaces of the particle separator two. The following sections describe the steps to obtain the presented results.

IV. RESULTS

A. Sample preparation

To corroborate the observed system, solid industrial samples were taken from the accretions formed inside the particle separators, as shown in Fig. 4. These samples were cut, roughened, and etched with a 12% sulfuric acid solution to reveal the flow lines of the formations of the different layers in the opposite direction of the gas flow entering the mouth of the cyclone separator.



(a) (b) (c)

Fig 4. Sample of gas flow accretion and creep lines (center), samples taken from the thinner incoming tail, Image (a) shows flow line and layers of deposited material when attacked with 12% sulfuric acid (side of the separator on the right edge) and the side of the gas to the left of the image (b), which shows the accelerations formed by the collision between particles, the image (c) shows the shape of the flow lines of the adhesions in the metallic crusts, at the point where the impact speed decreases. This proposed mechanism complies with thermodynamics and the process conditions for accumulations.

B. Proposed coefficient for iron oxide dust

Depending on the temperature range, the materials have a thermo creep constant McLean [9] 0-0.3 TM, 0.3-0.5 TM, 0.5-0.9 TM, and 0.9-1.0 TM. Where TM is the melting temperature of the pure element, in this case, iron; based on this information, the following graph was obtained.

Table 2. Comparison of obtained calculation results.

Temperature (°C)	K Termo Creep	Temp. Creep
461	0,3	460
700	0,5	767
1400	0,9	1381

C. Influence of temperature on the thermal adherence constant

The value of the adhesion coefficient in the temperature range between 600°C and 700°C oscillates between 0.478 and 0.514 with a correlation of 0.977 for ceramic materials. These values are based on the range of coefficients proposed by McLean for metals in a diffusion-controlled creep process to consider a similar flow in liquid metals. These values are assumed to be related to a combined effect of the working pressure on the temperatures, which also affects the particle velocity, gas molecular weight, and oxide properties, such as a plastic-activated stage for any sticking tendency.

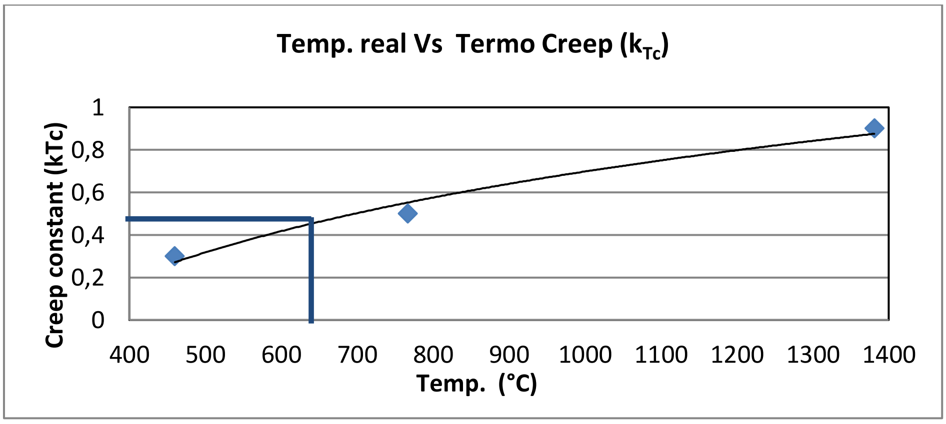


Fig. 5. Result of the thermo creep constant when working in a temperature range from 600°C to 700 ° C of 0.4784.

Once the operating temperature is obtained, the thermal creep constant is estimated. This value will be crucial to know the temperature for the mathematical simulator, as shown in equation 3. In this equation, KTc is represented as the constant of thermo creep, and Tr is the actual operating temperature in degrees centigrade. This gives a dimensionless value.

$$K_{Tc} = 0.5491 * \ln(Tr) - 3.095 \qquad (3)$$

Using the temperature difference mentioned above, for the occurrence of thermoplasticity in the considered system, in the temperature range 600 ° C (873K), to reach the melting point of the newly formed iron required, the value of the system's thermo-creep constant with a value of 0.478. This value represents a modification of the equation described by McLean applied to ceramic systems. Then, the modified equation to define the appearance of yield stress in the study system can be represented by Equation 4 and Figure 6.

$$Tc = 2.0921 * Tr - 1E\text{-}12 \qquad (4)$$

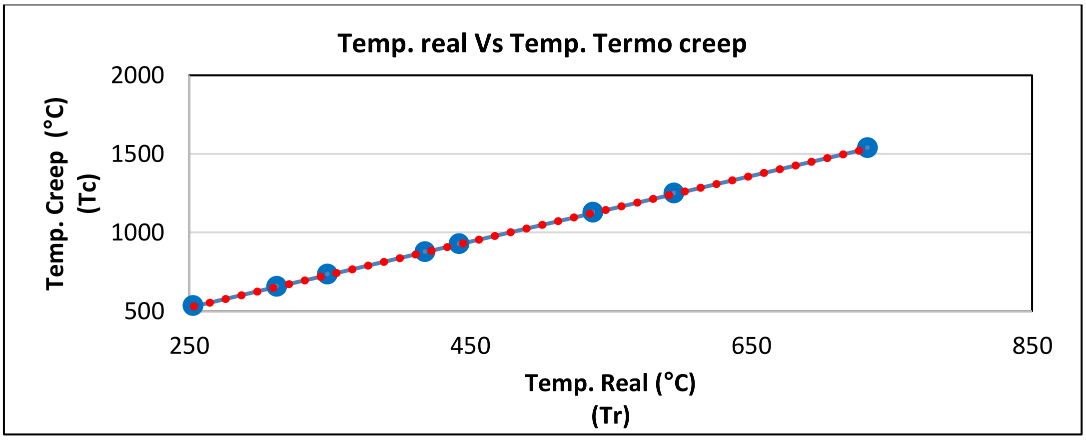


Fig 6. Formation of thermal adhesion as a function of accurate operating temperatures.

D. Activation energy in the study system

The formation of adhesions in the form of shells in the cylindrical zone in the range of temperature and pressure studied is possible in fluidized bed processes when working with molecular weights in the gas of 10 gr/mol. To develop the critical temperature for the thermoplasticity of the partially reduced particle, it is necessary to assume a specific temperature gradient between the hot gases and the solid particle. Therefore, this investigation took a difference of 30 degrees Celsius for heat transfer.

$$logK = \log A - \frac{E_A}{R} * \frac{1}{T} \qquad (5)$$

Figure 7 shows the thermal creep temperature on the vertical axis as a function of the thermal creep constant used to visualize the change in temperature as a function of the Arrhenius activation energy.

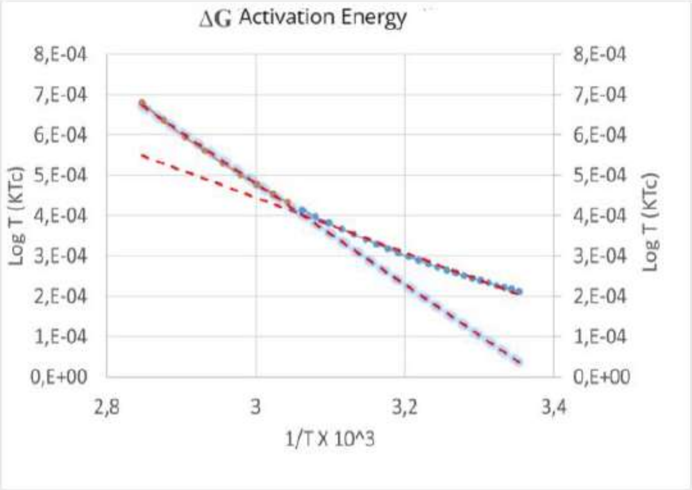


Fig 7. Activation energy through the Arrhenius relation
Diffusional Control CD; CQ Chemical control; CM Mixed Control

In the case of collided particles, the activation energy values for the temperature range studied help identify the predominant mechanism: dysfunctional control, mixed control, and chemical control.

The values obtained for the different mechanisms are as follows:

1.-Diffusinal Control
Log K = -0.013 * 1 / T + 0.0045 (6)
3.- Mixed Control
Log K = 0.052 * 1 / T + 0.0038. (7)
2. Chemical Control
Log K = -0.0008 * 1 / T + 0.0028

The influence of temperature can be worked by following the particle collision theory described by Arrhenius. In these graphs, chemical control is generated where the Bogging formation of accumulations in the bed can occur. The first hypothesis is rectified: a diffusion control where occurs sintering and finally, a mixed control is affected by the change in temperature and the constant of the thermal creep, the activation energy is of the dysfunctional control 5.949 Kcal/mol pending 1.3 X10^3; Chemical control 3,661Kcal / mol pending 0.8X 10^3 and mixed control 4.805 kcal/mol pending 1.05X10^3.

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CONCLUSIONS

1. The application of particle collision theory has helped determine the energies generated for the formation of adhesions in the particle separators in the range of 600 °C to 700 °C to determine the formation of fayalite in systems that combine the presence of ferrous oxide, silica and the presence of magnesium oxide.
2. The values of the adhesion coefficient for ceramic systems, such as the one studied. Within the temperature range between 600 °C and 700 °C, it oscillates between 0.478 and 0.514 with a correlation of 0.977. These values modify what Mc Clean proposes for metals by the range of coefficients presented and already indicated and are applied in a diffusion-controlled creep process to consider a similar flow in liquid metals for the case of thermospray.
3. This theoretical principle has made it possible to determine a creep temperature constant that modifies McLean theory for ceramic types of metals when the energy released inside the particle separator exceeds the transformation value of solid oxides to liquid and is sufficient so that the oxides studied are susceptible to thermo-viscosity and consequent plasticity.
4. The results summarize the summation of the energies released inside the cyclone separator, which is 660 KJ/mol higher than the 599 KJ/mol required to melt silicon oxide at 2000 ° C.
5. Applying the Arrhenius equation, it is possible to determine the activation energy for chemical (CQ), dysfunctional (CD), and mixed (CM) control. As a result, an activation energy of 5.94 kcal/mol CD, 4.81 kcal/mol CM, and 3.66 kcal/mol CQ with a total activation energy of 14.41 kcal/mol for the formation of fayalite, a value very close to the theoretical value.

RECOGNITION

The authors are incredibly grateful to the Graduate Research Directorate at UNEXPO Puerto Ordaz for the opportunity to carry out this research related to a focus on the thermoviscosity mechanism in the formation of fayalite-type ceramic accumulations in particle separators in CFD reactors that occur at temperatures below the eutectic point.

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