

Energy balance formation of sub-eutectoid fayalite at high pressures in particle separators

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Abstract: This article presents an approach to the problem of ceramic types adhesion, applying energy and matter balance to the established control volume (cyclone) with the use of mathematical formulas that are interrelated to develop mathematical calculations and establish a new mathematical model. The first results are obtained by operating the energy balance considering the collision of particles, using the principle of conservation of energy, the first law of thermodynamics, in order to obtain information that allows describing the phenomena of thermoplasticity and creep, in the formation of adhesions, from a physicochemical and kinetic point of view, which will serve as the basis for understanding their effect. As a result, an energy value of 660 kJ / mol was obtained, sufficient energy to start the transformation of the solid particles to a state of thermo-flow that allows the adhesion phenomenon to be started.

Keywords: Adhesion, energy balance, cyclones, elutriation, eutectoid, fayalite, thermoplasticity.

Balance de Energía formación de fayalita Sub-eutectoide a altas presiones en separadores de partículas

Resumen: En este artículo se presenta una aproximación al problema de la adherencia tipos cerámicas, aplicando balance de energía y materia al volumen de control establecido (ciclón), con la utilización de fórmulas matemáticas que se interrelacionan entre sí para desarrollar los cálculos matemáticos y establecer un nuevo modelo matemático. Los primeros resultados se obtienen operando el balance energético considerando la colisión de partículas, utilizando el principio de conservación de energía, la primera ley de la termodinámica, con el fin de obtener información que permita describir los fenómenos de termo-plasticidad y fluencia, en la formación de adherencias, a partir de un punto de vista fisicoquímico y cinético, que servirá de base para comprender su efecto. Como resultado se obtuvo un valor energético de 660 kJ/mol, energía suficiente para iniciar la transformación de las partículas sólidas a un estado de termo-fluencia que permite iniciar el fenómeno de adhesión.

Palabras Clave: Adhesión, balance energético, ciclones, elutriación, eutectoide, fayalita, termoplasticidad.



I.INTRODUCCIÓN

Indirect reduction processes that use the fluidized bed, such as the Finmet process, which operate at pressures greater than 5 bar and temperatures greater than 600 ° C, it is made up of a sequence of reactors that are inside each one of them. Four particle separators known as cyclones are located, as can be seen in figure 1.

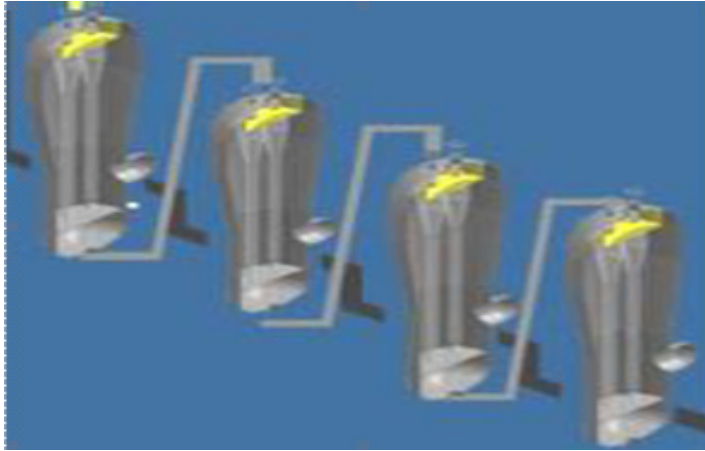


Fig 1: reactors with cyclones of the FINMET plant in Venezuela. Turnero Ruben 2010.

These cyclones for separating particles smaller than 50 μm (microns), are used for their simplicity of operation and low maintenance cost due to the absence of moving parts, avoiding effects of dissipation of mechanical energy in the discharge of a hydrocyclone (Bustamante, 2013), [1] the relationship of these variables are of empirical origin and are limited to the development of correlations using experimental data, taking into consideration the design of the device considered as a “Black Box” with the use of empirical models that are still unknown. [2], [3]. These models do not consider the phenomena that occur inside the cyclone. Currently, these models are based on the physics of the fluid that has allowed them to be used in circulating fluidized bed processes (CFD), therefore a large number of numerical solutions are required that make it difficult to process the data generated inside the container. The latest approximations obtained to seek a better understanding of the separation of the size of the particles as the only consequence of the movement of the fluid, for this reason, it allows to optimize the performance and the operating conditions by examining only the flow of the gas with solid.

The literature does not report the relationships between some variables associated with the number of solids at discharge to maintain the correct operation of the equipment, without taking into account the field of internal velocity on the discharge in an incipient manner [4], [5]. From the aforementioned, it can be established that even though there is evidence of the inlet and discharge flow, it has not been included in the performance of the equipment operation. For this reason, with the aim of coupling the separation dynamics by particle size, the energetic conditions that can be used to understand these phenomena inside the cyclone separator are considered.

These considerations generate lines of research that allow giving answers to the balance of internal energies associated with the phenomenon of adhesions in the cylindrical zone of the particle separators used in circulating fluidized beds.

This article has been divided into sections, as follows: a first approach to the balance of matter to explain the phenomenon of the interaction of the particle size when it enters the cyclone separator, then a theoretical approximation of the balance of mechanical energy inside the separator is presented cyclonic starting from Cauchy's law to later finish with the validation of the calculation that allows explaining the phenomenon of adherence and operability from the energetic aspects related to the conditions of formation of the shells on the walls.

ACTUAL WORK

Concept of thermal plasticity

Few authors have introduced the concept of thermoplasticity in particle sizes that go into motion in a cyclone

separator that is subjected to temperatures above 600 ° C. However, from the perspectives of the operation of the equipment, which involves the heat generated by the impact, heat by inelastic shock, heat by chemical reactions, differentiation from significant pressures, this could be definitely decisive inefficiency.

From a thermodynamic approach, the physical meaning of the energy released by a defined particle size within the separated particle could be established. As explained in [6] that starting from Cauchy's first law and multiplying both sides by the viscosity (ν).

$$\rho \frac{D}{D_t} \left(\frac{v^2}{2} \right) = (\nabla \cdot T) \cdot v + f \cdot v \quad (1)$$

If the body force f is expressed as the gradient of a potential it can be written as $f = -\nabla\phi$, and equation (1) can be rewritten like this:

$$\rho \frac{D}{D_t} \left(\frac{v^2}{2} \right) = (\nabla \cdot T) \cdot v + \rho \cdot \frac{D\phi}{D_t} \quad (2)$$

Rearranging the terms, we finally get that:

$$\frac{D}{D_t} \left(\frac{v^2}{2} + \phi \right) = (\nabla \cdot T) \cdot v + T : \nabla v \quad (3)$$

The product $T : \nabla v$ represents the viscous dissipation $E\nu$.

Cyclone mass balance

To perform the energy balance in a circulating fluidized bed reactor made up of a battery of cyclones arranged in a conical shape that internally allows the maximum separation of the solid particles found in the reducing gas stream, coming from the entrained gas bed. iron ore in wustitic thermodynamic stgte (FeO). (see figure 2) there is a schematic of the particle separator.

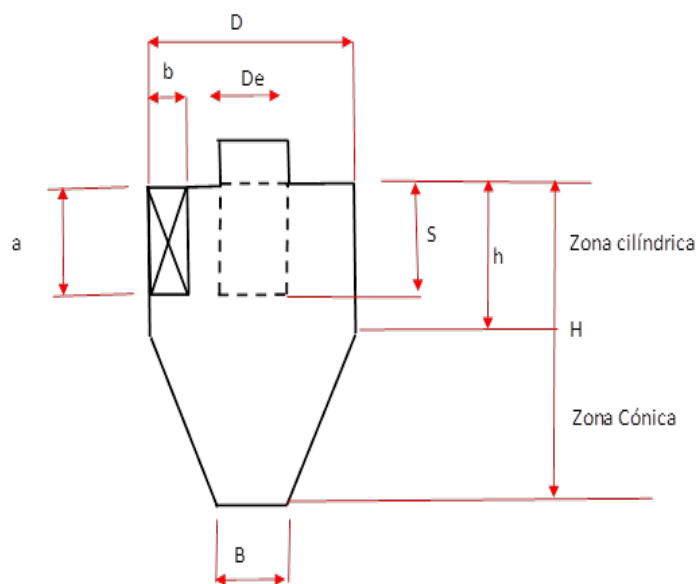


Fig 2: Schematic diagram of a particle separator (cyclone) Source: author 2020.

Data from the cyclones used in the FINMET process plant (Venezuela). See table I where the data used for the mathematical calculations in the cyclone is shown.

Table 1

Simbol	Significado	Unidad	Valor
D	Cyclone diameter	mts	1,423
De	Cylinder diameter	mts	0,508
B	Lower outlet diameter	mts	-
H	Cylindrical zone height	mts	-
h	Cylinder height	mts	1,391
S	Height of outlet cylinder	mts	25,57
a	Inlet height	mts	0,880
b	Inlet mouth width	mts	0,278

Source: Orinoco Iron cyclone plans.

For the calculations, the control volume is established, in this case the cylindrical zone of the cyclone is selected in which the mass and energy balances necessary to demonstrate its influence on the mechanism of adherence of the particles on the metallic surface of the cyclone walls, which causes the generation of shells that affect the operation of the particle separator.

Flow Characteristics

In the cylindrical zone of the cyclone a forced rotational flow is generated, causing the particles that enter the gas stream through the inlet, generating a friction force against the walls of the equipment, said inlet and outlet head loss is usually proportional to the square of the speed of the gas that circulates through the cyclone, through the Euler number (Eu) this magnitude can be related to equation 4.

$$E_u = \frac{\nabla P}{\rho_{gas} \cdot \frac{v^2}{2}} \quad (4)$$

Where

ΔP is the pressure drop between inlet and outlet.

ρ_{gas} is the density of the gas.

U is the velocity of the gas as it enters.

This velocity of the gas entering the cyclone is the superficial velocity based on the internal diameter of the cyclone. (see equation 5).

$$U = \frac{4 * q}{\pi * D^2} \quad (5)$$

Where

q is the volumetric flow rate

D is the internal diameter of the cylindrical zone.

The Euler number that relates pressure forces to inertial forces is practically constant for a cyclone of defined geometry.

Figure 4a describes how the particles that enter the cyclone make a circular movement towards the walls of the equipment. The net flow of the gas is radial towards the center of the tube, this force acting on the particles as described in figure 4b for a given radius of the orbit of movement, these particles are dragged (F_b), those of thrust (F_u) and the centrifuge (F_c), The drag forces occur towards the interior of the fluid, this is due to the fact that the gas flows into the cyclone, generating two components, the tangential velocity (U_{θ}) and the radial velocity (U_{r}).

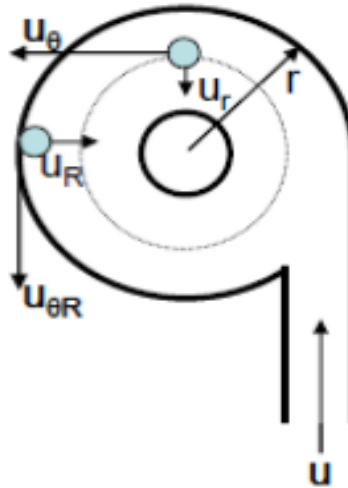


Fig 4 diagram of particle motion in a cyclone adopted by Rhodes 1998

The forces breakdown currently be considered are show in figure 4a, regarding the movement of the particles in the cylindrical zone are shown below.

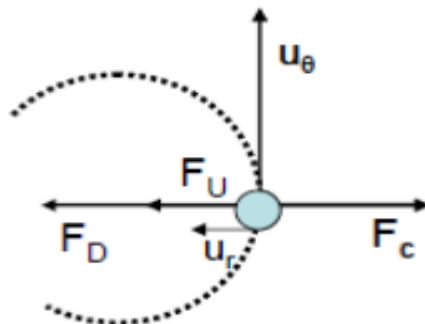


Fig 4 b balance of force on a particle adopted by Rhodes (1998).

The centrifugal acceleration (a_c) generated by the particle inside the cyclone when it makes a turn, is to provide the square of the tangential speed and inversely to provide the radius of the turn, see equation 6.

$$a_c = \frac{(U_{tang})^2}{r} \quad (6)$$

Considering that $F_c = m_p \cdot a_c$, where m_p is the mass of the particle x is the diameter of the particle, it results:

$$F_c = \frac{\pi * x^3}{6} * \rho_p * \frac{(U_{tang})^2}{r} \quad (7)$$

Similarly the pushing force can be written as:

$$F_c = \frac{\pi * x^3}{6} * \rho_{gas} * \frac{(U_{tang})^2}{r} \quad (8)$$

The drag force if we assume Stokes's law is valid and can be expressed as:

$$F_d = 3 * \pi * \mu * U_{rad} * r \quad (9)$$

As the particles move inward or outward until the force is swinging, at this point we can assume that the particles are in equilibrium in their orbit. In this you can verify.

$$F_c = F_d + F_u \quad (10)$$

$$\frac{\pi * x^3}{6} * \rho_{gas} * \frac{(U_{tang})^2}{r} = 3 * \pi * \mu * U_{rad} + \frac{\pi * x^3}{6} * \rho_p * \frac{(U_{tang})^2}{r} \quad (11)$$

$$x^2 = \frac{18 * \mu * r}{(\rho_p - \rho_{gas}) * (U_{tang})^2} * U_{rad} \quad (12)$$

Equation (12) indicates that small particles will be in equilibrium at radii close to the center of the cylinder, while the larger particles will be in equilibrium at larger radii. For this reason, the larger ones tend to be collected and the smaller ones carried away by the gas.

On the other hand, if the gas flow circulates radially as shown in figure 4a, it results:

$$q = 2 * \pi * r * L * U_{rad} = 2 * \pi * R * L * U_R \quad (13)$$

Where q is the volumetric flow rate of the gas, L is the height of the cylindrical section of the cyclone, r and R represent the radial coordinate evaluated at any r and $D/2$, while U_{rad} and U_R represent the velocity of the gas at any radius and at the area near the wall, respectively.

Substituting expressions (10) and (11) in (12) is obtained in equation 14.

$$x^2 = \frac{18 * \mu * r}{(\rho_p - \rho_{gas})} * \frac{(U_{tang})^2}{(U_{tang})^2 * R} * \left(\frac{r}{R}\right) U_{rad} * \left(\frac{R}{r}\right) \quad (14)$$

Rearranging the terms, it is as follows:

$$x^2 = \frac{18 * \mu * r}{(\rho_p - \rho_{gas})} * \frac{U_R}{(U_{tang})^2} * r \quad (15)$$

Where r is the equilibrium orbit of the particle of size x , in case the particles are not spherical, x is the dv . If it is assumed that the particles that can be collected are those that are close to $r = R$, it results:

$$(x_{crit})^2 = \frac{18 * \mu}{(\rho_p - \rho_{gas})} * \frac{U_R}{(U_{tang})^2} * R \quad (16)$$

x_{crit} represents the critical size; if the particles are smaller than x_{crit} they will not be collected and will be carried by the gas, otherwise they will be collected at the bottom of the cyclone. If the cyclone operation complied with all the hypotheses made to conclude in equation 16, the efficiency per class should be 0 for all particles smaller than x_{crit} and 1 for those with a diameter greater than x_{crit} .

III RESULTS ANALYSIS

ENERGY BALANCE IN THE CYCLONE

The algorithm to determine the energy balance is presented in several steps as shown below, for this reason it will start with the energy balance that acts inside the particle separator where the different energies will be studied: $Q_{impacto}$; $Q_{vacancia}$; $Q_{potential}$; Inelastic collision.

Identifying the input data in Table 2 to carry out the energy balance is to know how to see figure 5 where the diagram of the energy balance in the cyclone is shown table 2.

Table 2 variable inputs

Simbol	Significado	Unidad	Valor
ρ_{lecho}	Wustite bed density	kg/cm ³	1.543
P	Work pressure	bar	10
H_2	Hydrogen	%	57
CO	Carbon monoxide	%	8,95
CO_2	Carbon dioxide	%	3,30
CH_4	Methane	%	25,57
N_2	Nitrogen	%	4,13
$T_{entrada}$	Inlet temperature	°C	700
T_{salida}	Outlet temperature	°C	600
ρ_{Fe}	Iron density	kg/m ³	2,461
\emptyset	Reactor diameter	mts	4,5

Flow diagram for the energy balance in the cylindrical zone

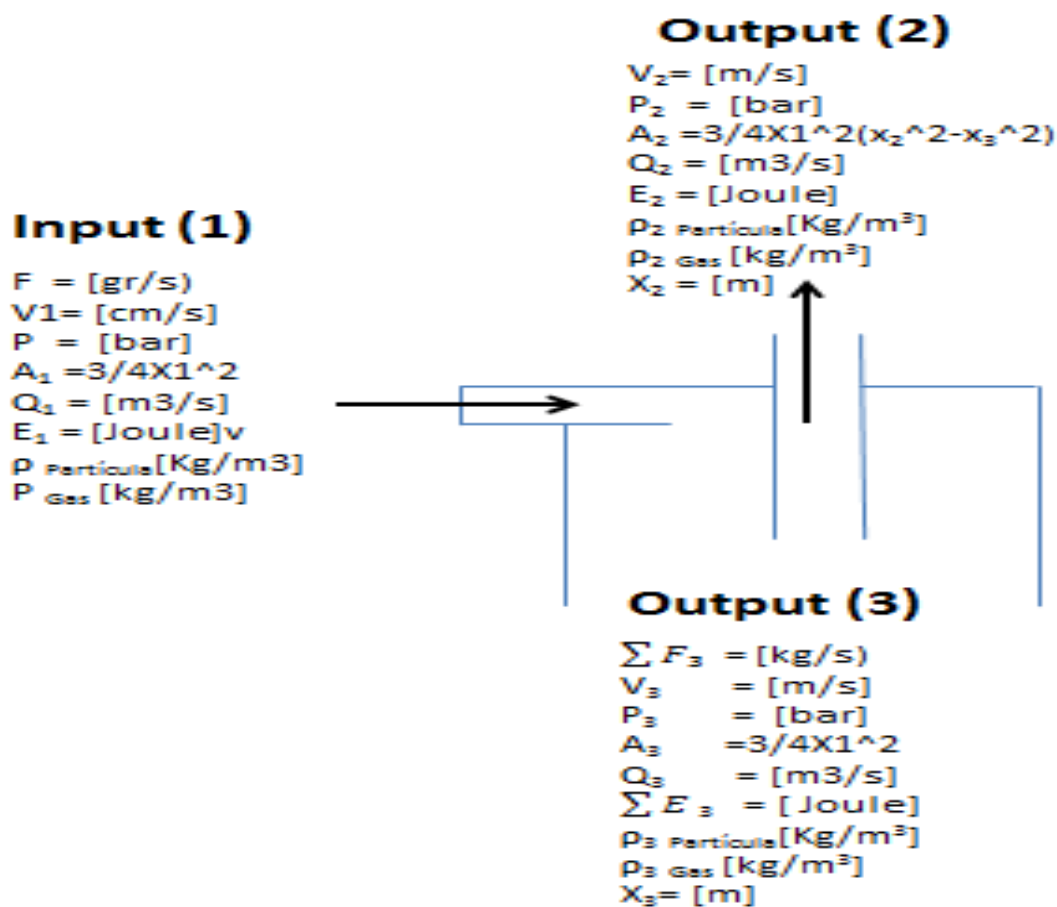


Fig 5 diagram to explain the energy balance in the cyclone. Source the author 2020.

Calculation of the molecular weight of the gas

Calculation of the molecular weight of the reducing gas (Kg/mol) Molar flow.

This is calculated by the percentage of the element times the molecular weight and divided by 100.

H₂ = 57gr / mol; CO = 8,95gr/mol; CO₂ = 3,30 gr/mol; CH₄ = 25,57gr / mol and N₂ = 4,13 gr/mol.

The molecular weight of the reducing gas is 10,37 gr/mol.

Calculation of the gas density using operational data

The reducing gas density kg / m³ is determined, applying the ideal gas law $P * V = n * R * T$, we can substitute the number of moles that is equal to the mass over the molecular weight of the gas. Then we have the equation of the following form $P*V= m/Pm*R*T$, now if we can clear the density of this equation, remembering that the density is equal mass over the volume, the mathematical equation is: $m/V=P*PM/R*T$ we already have the formula to calculate the density, for this we have the input data.

The molecular weight of the reducing gas that was calculated in step two is 10.37 gr/mol, the outlet gas temperature is 600°C, and the working pressure is 10 atm.

I convert 600 degrees centigrade to kelvin = 873 K

$$\rho = \frac{10,37 \frac{gr}{mol} * 10 atm}{0,0821 \frac{lbs*atm}{K*mol} * 973 K} ; \rho = 0,1715 gr/lts = 1,75 kg/m^3$$

Calculation of bed density

The density of the bed is calculated, for this the pressure data measured by the instrument pdi xy.18.733 is taken, which censes the density of the bed in a wustite reactor, in this case the value of 108 mbar, then it was transformed to density obtaining a value of ρ of 1,542 kg/m³.

Calculation of real velocity of the gas entering the cyclone separator

The speed of the gas that is entering each of the cyclones is determined, the inlet flow is assumed to be 200,000 Nm³/h, total flow that enters the reactor, from the bottom, this flow is divided by four since it is the amount of cyclones that make up the system, in order to have a uniform distribution.

$$Q = \frac{200.000 \frac{Nm^3}{h}}{4} ; 50.000 \frac{Nm^3}{h}$$

working pressure 10 atm and temperature of 600°C.

It is important to calculate the actual flow that is entering the cyclone.

Q_{real} is calculated with the following equation.

$$Q_{real} = \frac{200.000 \frac{Nm^3}{h} + \frac{1,013}{10 atm + 1,013} * (273,15 + 600^\circ C)}{273,15^\circ C}$$

$$Q_{real} = 58.806 \frac{m^3}{h}$$

Divide by 4 to determine the actual flow entering each cyclone.

$$Q_{real} = 14.701 \frac{m^3}{h}$$

This is actual flow that should enter the rectangular mouth of each cyclone.

Calculation of the theoretical entering gas velocity

We then proceed to calculate the velocity of the gas entering the cyclone, with the following flow equation, in which the velocity is cleared.

$$Q=V*A; V=Q/A$$

Where

V is the velocity m/s

Q is the flow rate m³/h

A is the area of the rectangular = 0,245m²

The theoretical and actual speed is determined.

Theoretical V = 56,77m/seg (very high)

Real speed = 16,69 m/seg (Real speed)

Volume calculation of particle separation in the cylindrical zone

The cyclone volume calculations were made to determine the mass with which the wustite mineral particles are impacting the cyclone wall.

For this reason, it is necessary to know the material of manufacture of the barrel or cylindrical area, in this case it is 304 stainless steel with the density of austenitic stainless steel AISI-304 whose density ρ_{steel} 7,980 Kg / m³ these plates have a thickness of 15 mm, height 1,391 m, diameter of the cyclone 1,423 m (D) radius 0,712 m.

Calculation of the cyclone perimeter

$$P = 2 * 3,1416 * 0,712 m$$

$$P = 4,470mts$$

Volume calculation $h * e * P$

h is the height mts

e is the thickness mts

P is the perimeter mts

$$V = 0,093 \text{ m}^3$$

Calculation of inlet wall mass

M = Volume * Steel density

$$M = 744,53\text{kg}$$

Calculation of particles impact released energy

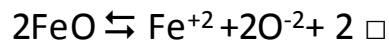
The impact energy is calculated with the following equation

$$E_c = \frac{1}{2} M * V^2$$

$$E_c = 103,707 \text{ K J / mol}$$

Calculation of energy for vacancies

The reduction chemistry is calculated: During the transition from wustite to metallic iron, 2 vacancies are generated, with this the amount of energy associated with the reduction mechanism is determined.



$$1(\square) = 28 \text{ cal/mol}; 1 \text{ J} = 0,238 \text{ cal /mol}; 1(\square) = 235,29 \text{ J}$$

The energy per vacancy product of the reaction of wustite with oxygen is calculated.

A vacancy is equal to 28.38 Kcal/mol Tesis Dr Oscar Dam [7].

During this process, two vacancies arise

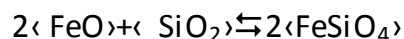
$$E_{vac.} = 4 * 28,38 \text{ Evac.} = 113,20 \text{ Kcal/mol}$$

$$E_{vac} = 473,63 \text{ K J/mol}$$

Determination of associated chemical reactions to calculate heat capacity.

Applying the first law of thermodynamics to explain the energy of formation of iron ferrosilicate in the proposed system.

For the formation of fayalite as expressed in the following reaction.



Next, in table III, we have the elements to be used to carry out the thermodynamic calculations

Table 3

Element	Molecular Weight (gr/mol)	Density (gr/cm ³)	Melting point (°C)
<i>SiO₂</i>	60	2,65	-
<i>FeO</i>	72	5,75	1.377
<i>Fe₂O₃</i>	160	5,24	-
<i>Fe₃O₄</i>	232	5,17	1.597
<i>2FeO.SiO₂</i>	203,78	(3,58 a 4,32)	1.205

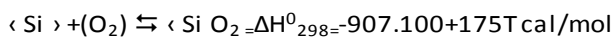
Source the author 2020

$C_p\text{Fe}(\alpha) = 37,12 + 6,147 \times 10^{-3}T - 0,5 \text{ J/K}$; $C_p\text{Fe}(\gamma) = 24,48 + 8,45 \times 10^{-3}T \text{ J/K}$

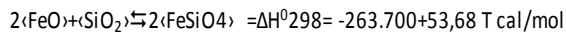
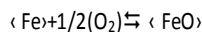
Thermodynamic reaction



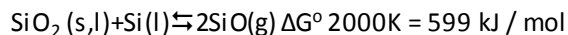
$\text{SiO}_2 \Delta H^0_{298} = -910.900 \text{ cal/mol}$



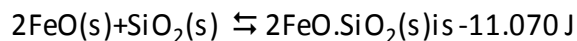
When the two reactions are combined:



Explains Eli Ringdalen, (2016) [8] Quartz (SiO_2) is the main source of silicon for the production of metallurgical grade silicon in submerged arc furnaces and with softening temperatures in the range of 1675 °C to 1800 °C, and melting temperatures in the range of 1790 °C to 1900 °C were recorded.



For the formation of fayalite David R Gaskell (2003) [9] in introduction to thermodynamics so that 2FeO.SiO_2 is a compound formed from FeO with SiO_2 at a pressure of 1 atmosphere, the free energy Gibbs, the following reaction is obtained.



The molecular weight is 203,73 gr/mol

$\Delta G^0_{1200K} = 54 \text{ KJ/mol}$

Therefore, 599 KJ/mol plus 54 KJ/mol are required to start the fayalite formation process; this gives a total of 653 KJ/mol.

Calculation of the heat capacity using the first law of thermodynamics

The heat of reduction reaction: It is the net heat in the passage from wustite to metallic iron, when the phase

transformation occurs Iron($\text{Iron}(\alpha-\gamma)$): This occurs after the impact of the particle with the metallic surface of the separator barrel mechanical cyclone, in this case the inlet gas temperature 600°C and outlet gas temperature 700°C are known, particle diameter \varnothing particle 4,31 E-04mm and the heat capacity is calculated with the following equation. The amount of energy transferred by heat between a sample of mass m of a material and its surroundings by a change in temperature from T_1 to T_2 is:

$$Q = \int_{T_1}^{T_2} C_p * dT$$

The energy transferred is calculated by applying the following equation $\Delta Q = C_p * m * \Delta T$ to determine the amount of heat transferred.

Where

ΔQ = Net heat transfer from gas;

C_p := Specific heat

m = Mass

The amount of energy released is determined.

$$C_p = 37,12 * (993,15K - 873,15K) + (6,17 * 10^{-3} * (993,15K^2 - 873,15K^2)) + 56,92 * (993,15K^{0,5} - 873,15K^{0,5}) + 24,48 * 10^{-3} * (1664^{-3} - 1187^{-3})$$

$$C_p = 5.948 \text{ J/K}$$

Calculation of particle volume

$$\text{Particle} = \frac{4}{3} * (1) * 3,1416$$

$$V_{\text{particle}} = 4,188 \text{ cm}^3$$

$$\text{Mass} = \text{Density} * V_{\text{particle}}$$

$$\text{Mass} = 4,32 \text{ gr / cm}^3 * 4.188 \text{ cm}^3$$

$$\text{Mass} = 18,096 \text{ gr} = 0.018096 \text{ kg}$$

The density of FeO 5,77gr / cm³ and the density of SiO₂ 2,62 gr / cm³ are known

Inlet temperature 600°C outlet temperature 700°C

The temperature in Kelvin 273,15 + °C

$$T_{\text{inlet}} = 873,15 \text{ K}$$

$$T_{\text{outlet}} = 973,15 \text{ K}$$

$$Q = m * C_p * \Delta T$$

$$Q = 12,92 \text{ KJ / mol}$$

Creep temperature when working with 600 °C,

$$T_c = 873/1808 = 0,478$$

$$T_c = 0,478 * T_f$$

Where

T_c is the critical temperature; T_f is the melting temperature of iron.

IV RESULTS

To carry out the energy balance, the composition of the gas that enters the wustite reactor with the following molecular weight 10,37 g/mol and working temperature of 600°C to 800°C with working pressures of 10 bar was taken.

Next, table 4 of the results of the energy balance that acts in the internal part of the cyclone separator is shown, in order to explain the adhesion formations and therefore the generation of the fayalite is possible.

Table 4

MEANING	UNIT (KJ/MOL)	UNIDAD (KCAL/MOL)
Energy per impact	103,71	29,79
Energy per vacancy	473,63	113,20
Energy per particle collision	12,92	3,09
Energy due to inelastic collision	69,75	16,67
Total Energy	660,01	157,74

Source: the author 2020

V.CONCLUSIONS

For the fusion of quartz in a liquid state at 2,000K, 599KJ/mol is required and for the fusion of fayalite at 1200K, 54 KJ/mol is required, the sum of energy gives a total of 653 KJ / mol with this amount of energy being is guaranteeing the formation of this ferrosilicate, by energy balance it was determined that 660 KJ/mol enough energy is generated to guarantee the softening point of the particles inside the cyclone separator.

The formation of adhesions in the form of shells in the cylindrical zone in the temperature range greater than 600 ° C and pressures greater than 10 bar, is possible in fluidized bed processes when they work with molecular weights in the gas of 10 gr/mol.

Thermoplasticity in the studied temperature range 600 ° C (873K) to reach the melting point of iron requires the following factor 0.478, obtaining the following equation $T_c = 0.478 * T_f$.

The results shown in the summary table of the summation of the energies released inside the cyclone separator is 660 KJ/mol higher than the 599 KJ / mol that is required to melt the silicon oxide at 2000 ° C.

RECOGNITION

The authors are especially grateful to the Directorate of Postgraduate Research at UNEXPO for the opportunity to write a research article related to the energy balance to explain the formation of fayalite inside the cyclonic separator that occurs at temperatures below the point eutectic.

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CURRICULUM SUMMARY



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