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Development of iron layers on the internal wall of reduction reactors

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Abstract

Refractory bricks are the most common materials used in equipments for carrying processes at high temperatures, such as the production of steel, cement and glass. These bricks are exposed to severe operation conditions, their life determines if an equipment should be stopped for reparation or replacement of the bricks. One of the phenomena that is present inside reactors or furnaces with an internal wall covered by refractory material is the formation of layers. As they growth, they cause disturbs in the product flow or at least decreases the reactor or furnace capacity, and in the worst case it is necessary to stop the equipment for major reparations. This work is centred in the formation of layers inside the direct reduction reactors. These layers are formed over the firebrick (Al_2O_3, SiO_2) wall from the Direct Reduced Iron (DRI) that is being processed in the reactor. The aim of this work is to describe the mechanism of formation and growth of these layers. We conducted several test for simulating the formation of layers by the application of shear stresses at high temperatures and under a reductive atmosphere to the a DRI pellet-refractory interphase. The amount of DRI adhered to the sample bricks was measured following an experimental design of nine independent variables. Temperature, shear stress and time were identified as important variables for the mechanism of formation and growth of the layers. Confirmation of the importance of these variables was determined by means of a proposal for avoiding the adhesion problem. This proposal consists in a treatment on the surface of the brick that minimizes the adhesion of DRI. The successful treatment of more than 6000 bricks for operating plants proves that our conclusions are correct.

1. Objectives

To identify which are the important variables and interactions that are responsible for the formation and growth of layers over the refractory brick on the wall of a DRI reactor.

To test several conditions at laboratory scale and industrial levels in order to confirm the importance of the selected variables and their mutual interactions.

To propose a mechanism that based upon the important variables explains how the formation of layers takes place.

2. Introduction

There are processes that are conducted inside reactors where the material that is being processed adheres to the wall forming layers. This phenomena is often presented inside moving bed reactors and rotatory kilns at industrial scale. Frequently the formed layer is an agglomerate that sticks to the reactor wall in a place where the conditions given by the stress, characteristics of the wall surface, temperature, composition and size of the particles reach critical values that allow the growth of this agglomerate on the wall. Generally, this phenomena becomes a trouble that implies availability losses in the plant, because they could either separate of the wall and close the material discharge, or keep adhered and decrease the reactor capacity (some of the layers are very resistant to deformation).

There have been several attempts for simulating at laboratory scale the layer formation on refractory walls. In this attempt, the temperature and normal stress were supposed high enough for forming the layers, but the layers did not appear because the shear stress was not considered.

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We present in this work the results of the tests run in equipment at laboratory scale that includes both normal and shear stress in the DRI-refractory interphase. With this equipment it was possible to reproduce the layer formation, and to have information for verifying that the variables and interactions found are indeed important. With this information we proposed a mechanism that was applied to the developing of a method to decrease the adhesion between the DRI and the surface of refractory, and therefore the layer formation.

We also validated a model that describes the kinetics of growth of the layer as a function of the temperature, shear stress and time.

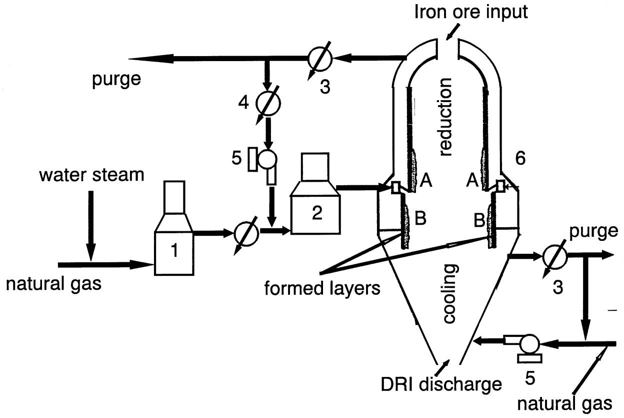

Fig. 1. Scheme of the direct reduction process. The main parts are: (1) reformer, (2) heater, (3) water condenser, (4) CO_2 absorber, (5) compressor, and (6) reactor. The layers are formed mainly at the A and B sites.

2.1. *The process*

One of the processes that are being used for the production of steel in the industry is the route called "direct reduction–electric arc furnace". The reactor (Fig. 1) is fed with pellet of iron ore that after the reduction with a reducing agent become "Direct Reduced Iron (DRI)" The reducing agent is produced by the reforming of natural gas and water steam in a device called reformer". The main equipments are: the reformer, gas heaters, CO_2 remover (by absorption), air compressors and the reactor itself.

2.2. *The reactor*

It consists in a shell made of steel and covered with refractory material that is in contact with either the iron ore or the DRI according to its position in the reactor. The reactor has an entrance plenum for the hot gas, and an exit plenum for the exhaust gas. The iron ore gets in by a port at the top of the reactor, and the DRI leaves it by an aperture at the bottom.

2.3. *The layers*

The layer formation takes place at points A and B in the reactor (Fig. 1) . The layers are made of agglomerate material and they can be as large as 15 cm thick and 2 or 3 m high. Some times they surround of all the reactor wall. The apparent density of the layers is approximately 4 g/cm^3, that is about 50% greater than the DRI particles, the chemical composition is basically metallic iron (greater than 83%).

2.4. *Adhesion mechanisms*

The simplest meaning of adhesion deals with the reversible work for separating two phases that initially have a common interphase. The most commonly reported mechanisms are:

1. Van der Walls forces.
2. Contact electrostatic potential.
3. Excess of electrostatic charges.
4. Magnetic attraction.
5. Liquid bridges.
6. Capilar pressure on the pores filled with liquid.
7. Union due to viscous agents.
8. Solid bridges.
   (a) salt crystallization.
   (b) curing of agglutinant material.
   (c) bridges due to solidification after having a liquid phase.
   (d) bridges due to sinterization.
   (e) bridges due to chemical reactions or diffusion due to concentration differences.
9. Mechanical anchorage.

These mechanisms were tested either theoretical or experimentally for selecting just the ones that are taking place in the process.

3. Strategy

The study of a complex phenomenon, such as the layer formation mechanism, brings in consideration many simultaneous variables that are affecting the whole process. In this case is advisable to use a partial experiment designs. These designs reduce the necessary time and cost of the experimentation because the number of experimental runs are reduced on the base of grouping some main variables. Both variance analysis and physical and chemical knowledge were used for identification of the most important groups. The first part of the work was to consider the variables that could control the layer formation process, at this moment we did not know which of them were important. We produced the layer at laboratory scale applying nine variables: normal stress, temperature, cement addition, pellet type, reduction degree, carbon content, rotational speed, residence time and the gas composition. The experimental design and the results of these tests are presented on Table 1.

According to Adamson [1] the effect of the shear stress over the adherence phenomena is about seven times greater than normal stress. This asseveration is by itself, very important; thus we decided to test it under our own conditions (Adamson used a pellet of steel over indium). We designed several devices for testing this hypothesis, from a bed of DRI pellets moved horizontally against a refractory brick (like those used for determining friction coefficients), to a single pellet in contact with a refractory specimen spinning over it.

Based on the obtained results in these devices we found that the best idea is to utilize a rotatory cell for achieving longer time of frictional contact between the pellets and the refractory (Fig. 2). The next step was the study of the adhesion mechanism by means of a microreactor specially designed (Fig. 3). Experimental procedure and the results obtained from these equipments are presented in the following sections.

3.1. Experimental procedure

3.1.1. The rotatory cell

For proving the importance of the shear stress, we designed a procedure for applying shear stress to a pellets bed (Fig. 2) The charge itself is moving the refractory specimen against the pellets in order to compensate the wear of them.

The refractory specimen was obtained by cutting an appropriate portion from a refractory brick. The bed of pellets is prepared with DRI pellet with diameters between 9.5 and 15.9 mm. In some tests the pellets were covered with cement in a suspension of 15 wt% of grey cement and 100 parts of water. The system was maintained under an atmosphere of nitrogen until the desired temperature was achieved, then the pellets were placed inside the reactor over the refractory specimen and the test started at the moment that nitrogen is substituted by a reducing gas, and the angular speed was fixed. The pellets in contact with the refractory were under shear stress that was coming from the normal charge that was being applied. The spinning speed was chosen in such a

Table 1
Experimental design and results of the tests

Experiment no.	Gas type	Cement coat	Pellet type	Met (%)	C (%)	Speed (rpm)	Time (min)	Stress (kg/cm^2)	Temperature (°C)	Layers (μg)
1	CO	Yes	Alzada	95	3.5	0	1	3.1	950	0.2
2	H_2	Yes	Alzada	95	0.1	30	1	3.1	950	76.8
3	H_2	Yes	Alzada	95	3.5	0	30	0.1	600	0.1
4	CO	No	Peña	85	3.5	30	1	3.1	950	14.7
5	CO	Yes	Alzada	85	3.5	30	30	0.1	950	0.1
6	CO	No	Peña	95	0.1	30	1	3.1	600	0.3
7	H_2	No	Peña	85	3.5	30	30	0.1	600	0.0
8	CO	Yes	Peña	85	0.1	30	30	3.1	950	29.7
9	H_2	No	Alzada	85	3.5	0	1	0.1	950	0.0
10	H_2	No	Peña	95	0.1	30	30	0.1	950	0.6
11	CO	No	Alzada	95	0.1	0	30	3.1	950	1.9
12	H_2	No	Alzada	85	0.1	30	30	3.1	600	45.7
13	H_2	Yes	Alzada	85	0.1	0	30	0.1	950	0.2
14	CO	Yes	Alzada	85	0.1	0	1	3.1	600	0.0
15	CO	Yes	Alzada	95	0.1	30	30	0.1	600	2.1
16	CO	Yes	Peña	95	3.5	30	30	3.1	600	7.1
17	CO	Yes	Peña	85	3.5	0	1	0.1	600	0.0
18	CO	No	Alzada	95	3.5	30	1	0.1	600	0.7
19	H_2	Yes	Peña	95	3.5	30	1	0.1	950	1.8
20	CO	No	Peña	95	3.5	0	30	0.1	950	0.0
21	CO	No	Alzada	85	0.1	30	1	0.1	950	0.4
22	H_2	No	Peña	95	3.5	0	1	3.1	600	0.0
23	H_2	Yes	Peña	95	0.1	0	30	3.1	600	0.0
24	H_2	Yes	Peña	85	0.1	30	1	0.1	600	0.8
25	CO	No	Alzada	85	3.5	0	30	3.1	600	0.5
26	H_2	Yes	Peña	85	3.5	0	30	3.1	950	0.0
27	H_2	No	Peña	85	0.1	0	1	3.1	950	0.3
28	H_2	No	Alzada	95	3.5	30	30	3.1	950	112.3
29	H_2	No	Alzada	95	0.1	0	1	0.1	600	0.0
30	CO	No	Peña	85	0.1	0	30	0.1	600	0.0
31	CO	Yes	Peña	95	0.1	0	1	0.1	950	0.0
32	H_2	Yes	Alzada	85	3.5	30	1	3.1	600	3.3

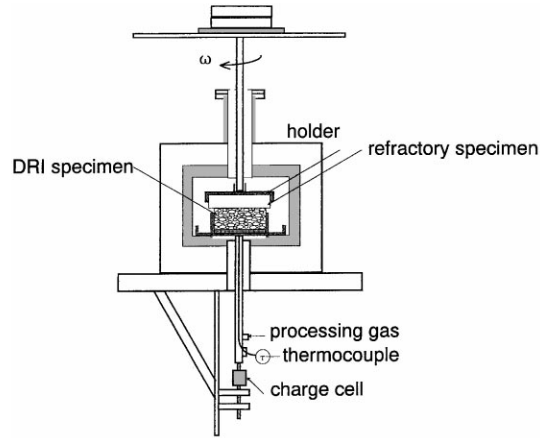

Fig. 2. Scheme of the rotatory cell.

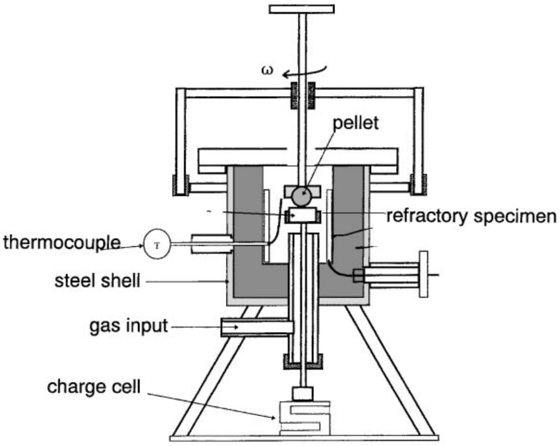

Fig. 3. Scheme of the microreactor.

way that tangential speed is about the same that typically we found inside the reactor when the DRI is flowing during the process. Operation conditions were maintained as long as needed. When the test finished the normal charge was removed and the reducing gas was substituted by nitrogen, when temperature was about 70°C or less both the pellets and the refractory were removed from the reactor. Metallic iron and dust formed during the test were separated by magnetic means. All of the materials were analyzed as described in the results section.

3.1.2. The microreactor

The rotatory cell allows to produce a layer, however for studying the adhesion mechanism is more adequate to take a single pellet instead of a bed. Such device is presented in Fig. 3. The variables that can be controlled are the same than in the rotatory cell, and the procedure of test is the same.

4. Results

4.1. Adhesion mechanisms

The adhesion mechanism that can occur in similar processes have been described by several researchers [2–18]. In the iron ore reduction process just some of those mechanisms take place.

In the introduction section were enlisted the possible mechanisms for forming a layer, argumentation that is presented below allows to discard the mechanisms that are not taking place.

Mechanisms related with Van der Walls forces, contact electrostatic potential and excess of electrostatic charges could give the reason for having fine material close to the wall, even when other possibility was a combination with bridges due to chemical reactions or diffusion due to concentration differences, and mechanical anchorage.

Magnetic attraction was eliminated because the refractory is not a magnetic material and the iron temperature is higher than Curie point.

Liquid bridges, capillary pressure on the pores filled with liquid and unions due to viscous agents were discarded because at operation temperature there is no liquid phase.

Salt crystallization and curing of agglutinant material were not taken because they demand an external agent while bridges due to solidification after having a liquid phase or bridges due to sinterization need a continuous union between the DRI and the refractory (this union does not exist, as shows). Although mechanism related with bridges due to sinterization should not be discarded for the layer growth (after layer formation).

Plates 1–3 show a 5 microns zone in the refractory next to the interphase; these photos show a layer formed in an industrial reactor after 1 year of operation, the calcium concentration is lower inside the brick, meaning that the calcium diffusion was from the brick to the layer. On the other hand potassium diffusion was from the layer to the brick, meaning that bridges due to chemical reactions or diffusion due to concentration differences were present.

Plates 4 and 5 show the layer that was obtained in the laboratory where the concentration differences found in the industrial layer did not appear. Since we got the layer, this means that the diffusion is not the direct mechanism responsible of the anchorage and that is rather a secondary mechanism.

Mechanical anchorage was accept because we found intimal contact between the refractory brick and the DRI. This was observed in either the industrial layer as in the laboratory layer. In both layers there is a chemical separation of the iron in each side of the interphase, but an intimate contact between the DRI and the refractory is always existing.

Sinterization takes place because the DRI particles are adhering and decreasing the porosity while they are increasing the resistance, in such a way that they are about 50% stronger that the DRI (Plate 6 and Plate 7).

Normal charge gives a normal stress of 3.1 kg/cm^2 in the industrial reactor and 0.1 kg/cm^2 in the pilot plant. From Rumpf equation [19] the punctual forces between the particles in a compacted bed as a function of porosity, coordination number and stress over the bed were calculated. Our calculations show that the stress over actual contact points are between 250 and 2500 kg/cm^2. From our own experience in the briquetting plant we

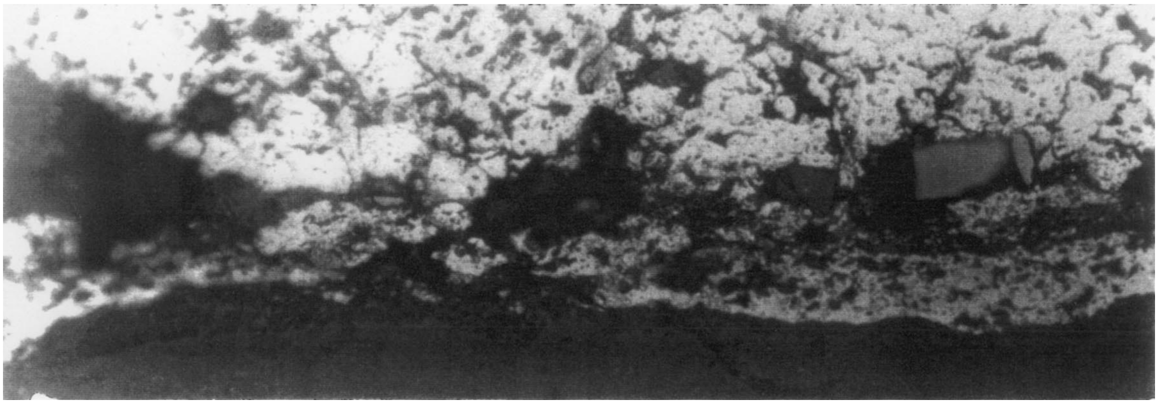

Plate 1. Aspect of the interphase in an industrial layer.

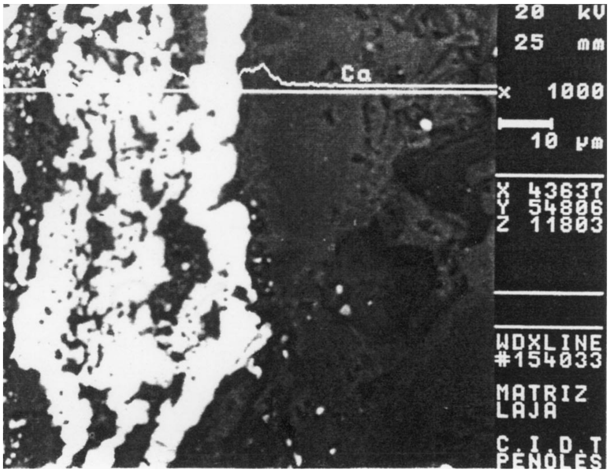

Plate 2. Mapping of calcium in an industrial layer.

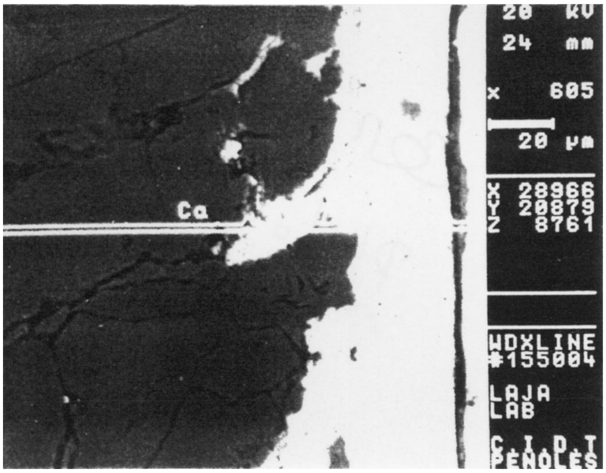

Plate 4. Mapping of calcium in a laboratory layer.

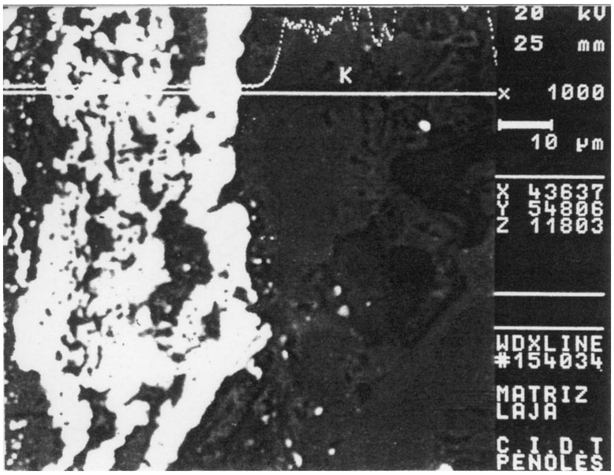

Plate 3. Mapping of potassium in an industrial layer.

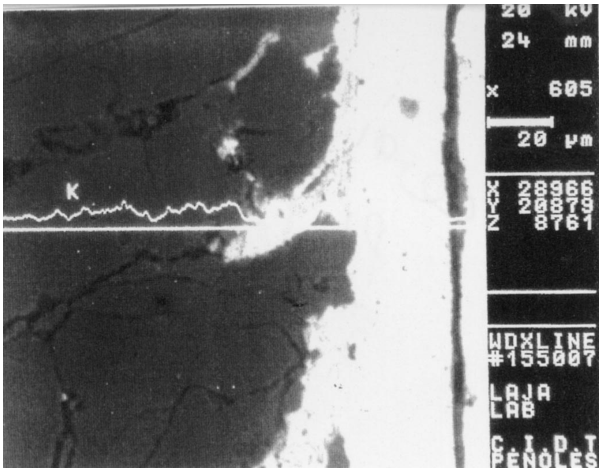

Plate 5. Mapping of potassium in a laboratory layer.

know that DRI flows plastically at temperatures around 650°C and pressures of 1000 kg/cm^2. These phenomena most occur in the contact point between the pellets and the refractory.

Table 2 shows the porosity and the chemical analysis of the refractory bricks. Average porosity of DRI is 60%. In Table 3 are presented the variance analysis based on the results of Table 1. The variables are: *gas* type (H_2 or CO), *cement* application (yes or no), *pellet* type (Alzada or Peña Colorada), *carbon* contain in pellet (0.1 or 3.5%), *metal*ization degree (85 or 95%), angular *speed* (0 or 30 rpm), experimentation *time* (1 or 30 min), normal *stress* (0.1 or 3.1 kg/cm^2), *temperature* (600 or 950°C). For the variance analysis [20] freedom degree is equal to 1 in all of the cases, and P (Table 3) is the probability of having a mistake in one variable or important interaction. Variables between parenthesis mean that measured effect corresponds to the sum of the variables inside the parenthesis, but it was taken the most consistent in agreement with previous experience in the plant. Variables in ***italic bold type*** in Table 3 are the ones that are important as the analysis presented in Fig. 4 shows. This figure presents a Pareto's graphic of the effect of the each variable an interactions over the response variable (the mass of DRI adhered over the refractory). It is possible from here to conclude that the presence of shear stress that is obtained with the spinning of the sample and the normal charge are the most important variables, taking into account the result over the dependent variable (mass of layer), after these vari-

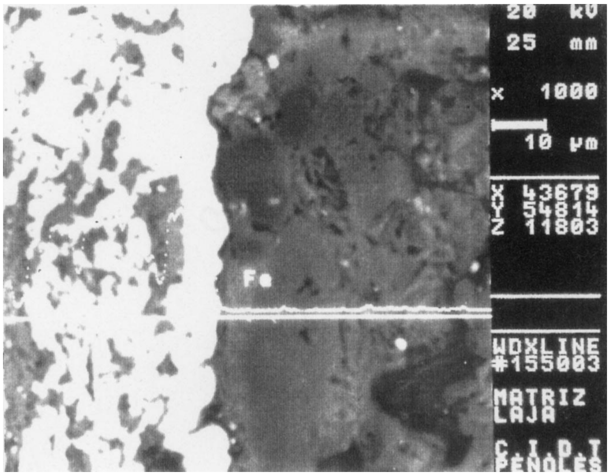

Plate 6. Mapping of calcium of iron in an industrial layer.

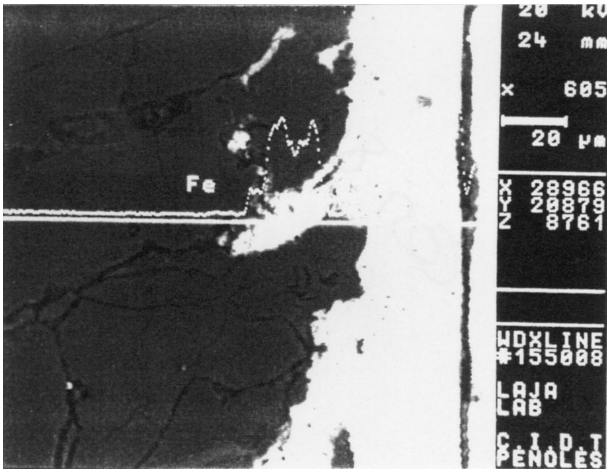

Plate 7. Mapping of iron in a laboratory layer.

Table 2
Porosity and chemical analysis of the refractory brick

Apparent porosity	11—15%
Density	2.26—2.36 gr/cm^3
SiO_2	51—55%
Al_2O_3	42—45%
Fe_2O_3	1.5—2.5%
CaO	0.2—0.8%
MgO	0.5% maximum
TiO_2	1.2—2.2%
Na_2O+K_2O	0.5—1%

Table 3
Variance analysis

Variable	Square sum	*F*	*P*
Pellet, speed, stress	1060.3	5019.2	0.009
Pellet, time, stress	95.2	450.8	0.030
Pellet	1116.3	5284.2	0.009
(metal) (***pellet, stress, temperature***)	365.9	1731.8	0.015
Carbon	10.1	47.9	0.090
Speed	2686.4	12716.9	0.006
Time	318.8	1509.0	0.016
Stress	2556.1	12100.0	0.006
Temperature	994.6	4708.1	0.009
Speed, time	291.6	1380.4	0.017
Speed, stress	2464.0	1164.0	0.006
Speed, temperature	950.5	4499.3	0.009
Gas, carbon	0.6	2.6	0.348
Pellet, stress	1106.9	5239.5	0.009
Pellet, speed, time, stress	80.6	381.8	0.032
Pellet, speed	1055.7	4997.4	0.009
Pellet, speed, stress, temperature	349.8	1655.9	0.015
Time, stress	326.4	1545.1	0.016
Cement, metal	0.0	0.0	0.952
Speed, stress, temperature	968.0	4582.3	0.009
Pellet, time	120.1	568.6	0.026
Metal, time	4.8	22.8	0.130
Stress, temperature	1008.0	4771.6	0.009
Pellet, carbon	0.1	0.5	0.620
Pellet, temperature	316.3	1497.1	0.016
Speed, time, stress	306.3	1449.9	0.016
Pellet, time, temperature	6.8	32.4	0.109
Pellet, speed, temperature	298.9	1414.9	0.017
Metal, speed, time	7.2	34.2	0.106
Pellet, speed, time	99.4	470.6	0.029
Total error	0.2		

ables are (in order of importance) the pellet type, temperature and time. For confirming that the most important variable is the shear stress, we proposed a treatment for decreasing it and observe the deposited mass on a brick after this treatment. The idea is to have a smooth surface with less porosity (less sharp edges and holes) and verify if the layer formation decreases.

In order to decrease the contact area between pellets and refractory and for removing the sharp edges and holes we tried several ideas. One of them was the smelting of the brick surface, removing the excess of material for having a smooth surface, and finally heat with an oxidant flame that smelts edges and the material inside the pores. Other tries were the addition of several common materials (Table 4) as is described below.

The procedure for testing the treatments consists in preparing ground (100 mesh) samples of the materials that are going to be applied to the brick (sand, alumina, white cement, lime, dust of silica–alumina brick, magnesia and grey cement) Bricks were perfectly clean with no trace of DRI. These materials were prepared in a water suspension in such a way that it was possible to put it over the brick and fill the pores, right after this the surface of the brick was heated with the torch for having a surface without sharp edges and holes. Several tests were conducted according to the experiment design shown in Table 5. These treated specimens were placed in the devices described above (the rotatory cell and the microreactor). Statistical analysis of the results (including the non parametric test of Krustall–Wallis due to a small sample size and different variances) was done. Table 6 shows the mass of DRI adhered to the surface. In conclusion with a confident level greater than 95%, sand is the material that is adequate for covering the surface bricks. Plate 8 is an example of the surface of a brick without treatment while Plate 9 shows the surface of a treated brick.

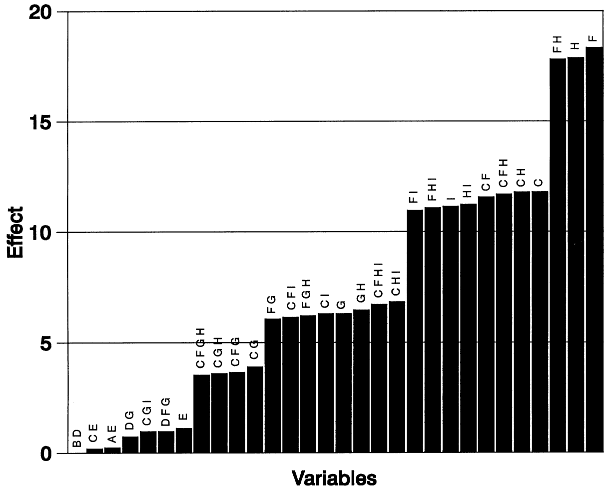

Fig. 4. Pareto's graphic of the variables effect. The bars represent the difference between the mass of layer obtained (average) with the high values of the selected variable or interaction and the obtained with the low values.

Table 4
Chemical analysis of the used materials for the brick's treatments

Compound	Sand	Alumina	White cement	Lime	SAB[a]	Magnesia	Grey cement
Fe_2O_3	1.40	3.69	0.56	0.27	1.11	0.41	3.64
SiO_2	95.20	13.52	19.98	0.83	52.44	6.40	19.08
MgO	0.04	3.65	1.21	1.06	0.21	87.16	2.4
CaO	0.08	1.04	65.21	65.21	0.40	1.56	63.66
Al_2O_3	1.62	78.14	5.41	1.16	43.23	1.98	4.95
Na_2O	0.23	0.0	0.17	0.04	0.36	0.03	0.63
K_2O	1.23	0.0	0.01	0.0	0.07	0.35	0.45
PXC	0.28	0.0	3.42	28.76	0.22	1.45	5.48

[a] SAB, Dust of silica—alumina brick.

Table 5
Experimental design of the brick's treatments conditions that form layer

Treatment	Description
T1	Smelt the surface of the brick without additive addition
T2	Addition of SAB and smelt the surface of the brick for closing pores
T3	Addition of lime and smelt the surface of the brick for closing pores
T4	Addition of magnesia and smelt the surface of the brick for closing pores
T5	Addition of grey cement and smelt the surface of the brick for closing pores
T6	Addition of white cement and smelt the surface of the brick for closing pores
T7	Witness brick (without any treatment)
T8	Addition of alumina and smelt the surface of the brick for closing pores
T9	Addition of sand and smelt the surface of the brick for closing pores

Operation conditions for testing each treatment

Temperature/time	9500°C/30 min
Normal stress/angular speed	3.1 $kg/cm^2$30 rpm
Carbon content	$\leqslant 0.1\%$
Metallization degree	$\geqslant 95\%$
Pellet type	Alzada
Gas type	H_2

Table 6
DRI adhered to each of the treated specimens (mg)

T1	T2	T3	T4	T5	T6	T7	T8	T9
3.2	0.6	11.0	23.3	87.7	12.9	6.8	1.5	0.1
120.8	0.4	2.0	24.6	6.8	15.7	22.3	2.8	0.1
8.3	0.1	69.5	21.4	21.0	59.2	18.8	4.7	0.0
65.0	0.6	34.0	7.2	13.9	17.3	2.9	2.1	0.5
23.9	0.4	0.7	7.0	88.2	6.5	5.1	8.8	0.0

With all of the above information it was proposed that the mechanism for starting a layer is that powder of DRI that is close to the refractory brick is extruded into the pores and cracks of the followed by sinterization that allows the growth of the layer. This mechanism would provide the necessary anchorage and explains the initial stage of growth. The pellet is soft and porous, and some of these pellets broken due to shear stresses against the edges of the reactor given powder that produces the layer as was explained above.

4.2. *Model for the layer growth*

With the treatment for decreasing the adhesion of DRI described above, it is clear that the mechanism that was here proposed is correct. However, this mechanism describes just the beginning of the formation of a layer. In a plant the variation of the pellet properties is wider than in the laboratory, but if the mechanism is correct the analysis in an industrial plant should give the same variables than the laboratory test. In this case we proposed a functional relation between the temperature, stress and time (which are the important variables) for calculating the adhered mass as the dependant variable. The correlation found is an Arrhenius type, the magnitude of the exponent is in good agreement with the values proposed by Nagao [21–24] suggest a physical mechanism such as the plastic deformation.

The tests for calculating the parameters were conducted in the same devices were the importance of the variables was evaluated. The independent variables were the same that we confirmed that were important: stress, temperature and time. The tests conditions are presented in Tables 7 and 8.

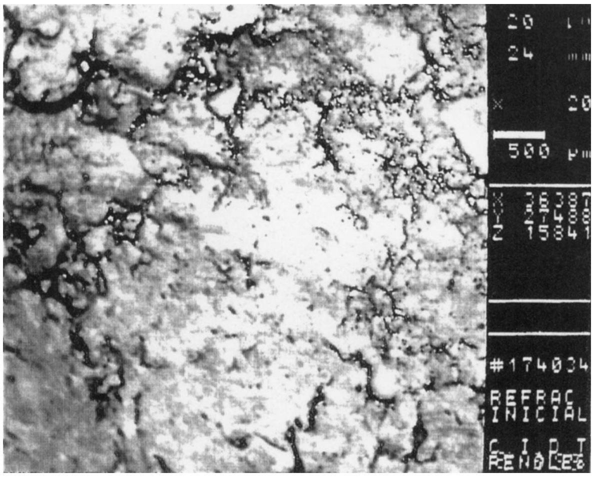

Plate 8. Surface of a brick without treatment.

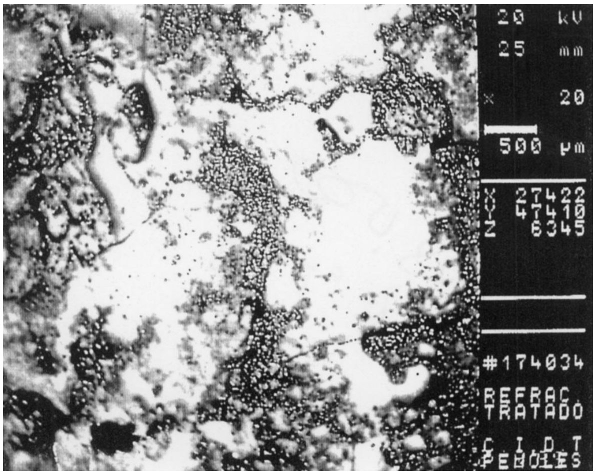

Plate 9. Surface of a treated brick.

Table 7
Operation conditions in the microreactor

Temperature/time	According to Table 8
Normal stress/angular speed	According to Table 8/30 rpm
Carbon content	1–3%
Metallization degree	Average of 90%
Pellet type	Alzada
Gas type	75% H_2/25% CO

Table 8
Experimental design and results of the tests applied to the proposed model. These tests were carried out in the microreactor

Experiment	Normal stress (kg/cm^2)	Time (min)	Temperature (°C)	Layer mass (mg)
1	3.1	15.5	600	0.9
2	3.1	30	600	3.2
3	1.6	15.5	775	0.7
4	0.1	1	600	0.2
5	0.1	30	950	0.4
6	3.1	30	775	4.7
7	1.6	1	950	2.3
8	0.1	30	775	0.8
9	3.1	15.5	775	4.8
10	0.1	30	600	0.2
11	0.1	1	950	0.1
12	1.6	15.5	950	1.1
13	0.1	15.5	950	1.5
14	1.6	1	600	0.2
15	0.1	15.5	600	0.2
16	3.1	30	950	2.6
17	1.6	1	775	1.2
18	1.6	30	775	5.1
19	3.1	1	600	1.1
20	3.1	15.5	950	7.1
21	1.6	15.5	600	2.0
22	3.1	1	775	0.7
23	1.6	30	600	0.3
24	0.1	15.5	775	0.2
25	3.1	1	950	1.2
26	1.6	30	950	3.3
27	0.1	1	775	0.1
28	1.6	1	950	0.9
29	1.6	30	775	1.3
30	3.1	15.5	950	9.5

Tables 9–11 show the statistical results that confirmed again that the selected variables that were important in the anchorage mechanism are also important for layer growth. Table 11 shows the calculated coefficients in the variables of the model. These three variables are important because they explain 69% of the behaviour of the layer growth. Taking into account the complexity of the whole process, the material processed in the actual plant is a mix of pellets with different properties (Alzada/Peña Colorada pellets), this 69% is quite acceptable. The obtained equation for calculating the mass adhered to the surface is:

$$M = 99.5\sigma^{0.6} e^{-\frac{5989}{RT}} t^{0.32} \qquad (1)$$

In this equation T is the temperature (K), σ is the normal stress (kg/cm^2) , t is time (min), M is the layer mass (mg) and R is the gas constant. Fig. 5 shows the observed data against the calculated ones by means of Eq. (1). Fig. 6 shows how important are these variables for the layer formation process.

In order to be sure that the results obtained in the laboratory and in the microreactor were valid at industrial scale, the treatment of surface bricks was conducted at industrial scale with a device specially designed, the procedure was as follows:

The refractory powder was applied to the surface of the brick for closing the pores, the excess of material was removed and the brick was placed over a sliding table. The moving speed was fixed to a value between 0.5 and 2.0 cm/s. The torch burns acetylene at a rate of 6 litre/min with 15 litre/min of oxygen. Separation between brick and torch was adjusted continuously. Once the bricks were treated they were installed in the reactor.

Table 9
Statistical analysis of the model

	Square sum	Freedom degree	Medium squares	F	P
Model	34.46	3	11.49	22.46	0.0
Error	13.29	26	0.51	–	–
Total	47.75	29	–	–	–

Table 10
Statistical analysis of the variables

	Square sum	Freedom degree	Medium squares	F	P
Stress	23.44	1	23.44	45.85	0.0
Time	6.22	1	6.22	12.16	0.0018
Temperature	4.80	1	4.80	9.38	0.0050
Model	34.46	3	–	–	–

Table 11
Statistical analysis of the coefficients of the model

	Coefficient	Standard error	t value	P
Constant	4.6	0.97	4.77	0.0001
Stress	0.60	0.09	6.57	0.0
Time	0.32	0.09	3.58	0.0014
Temperature	−3014	984	−3.06	0.0052

$r^2 = 0.69$.

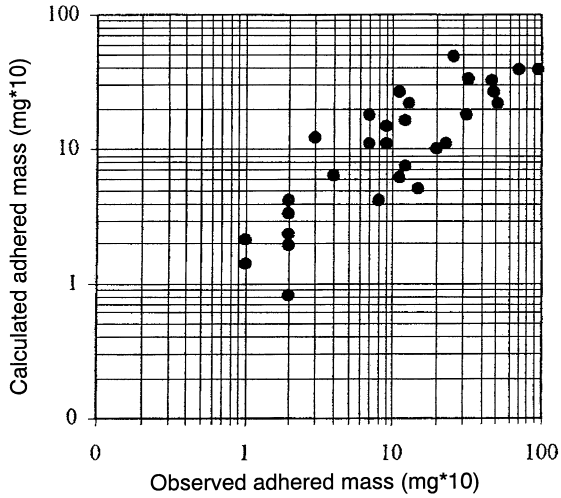

Fig. 5. Plot of the calculated adhered mass (mg×10) against the observed one.

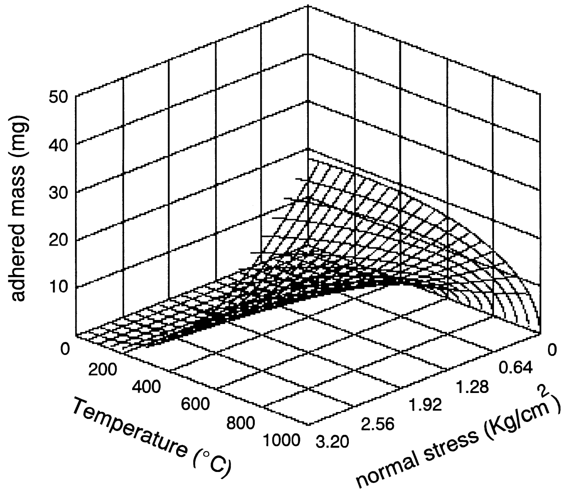

Fig. 6. Adhered mass as a function of the temperature and the normal stress. Notice their importance on the layer formation process.

5. Discussion

5.1. Regarding with the mechanism

The hypothesis of this work accepts that the shear stress is an important factor over the mechanism of layer formation in a laboratory scale. The results shown confirm the importance of this statement. Once that the layers were obtained in a laboratory scale, we conducted an experimental design for determining which were the important variables and interactions. By means of experimentation it was demonstrated with a confidence level greater than 95% that other factors are part of the mechanism, but the most important is the shear stress. The necessary experiment for separating all of the variables is $2^9 = 512$ tests, this is rather impractical thus we selected and manipulated the variables that according to the statistical results and the theory were more promising. Once that was demonstrated that the shear stress is really important we searched for the other variables that in combination with the shear stress were consistent (i.e. the pellet type was selected because it is logical that a plastic pellet will generate more area at the moment of deformation, the temperature was selected because the pellet plasticity depends of the temperature). Thus by means of physical-chemistry and statistics it was demonstrated that the heavy variables are the movement, the normal stress, the time, the temperature and the pellet type. In the table of variance analysis it was justified that they were the most consistent with the laboratory, the pilot plant and the industrial plant. Taking as a base the selected variables and interactions the anchorage and growth mechanism can be described as follows:

The fine material is extruded through the pores or cracks over the surface of the brick because of the shear stress. After this the sinterization of DRI takes place over the surface, decreasing the porosity and getting more resistant. The tension strength of sintered pellets is as high as 70 kg/cm^2. Taking into account the actual area in contact with iron over the brick (around 10%), this is more than enough for holding the layer just formed. The DRI of the new layer and the iron inside the porous are now anchored between them. The growth process follows to the initial anchorage due to the DRI powder that is being sintered over the first layer. This DRI powder comes from the pellet that is being braked while the moving bed is passing through the reactor. The preferred places for having layer formation are those where the shear stress is higher (Fig. 1) and where the temperature is higher. The growth mechanism is self fed because any edge on the reactor wall is a site were the stress is concentrate and so the pellet gives more fine material for the layer growth. Once that the material is inside a pore the only driving force for the anchorage is the surface energy, because the contact pressure can not be applied inside the pore. The shear stress and the sinterization are acting in series, while during the growth they act simultaneously.

5.2. Regarding with the treatments

The mechanism described above allowed to propose thermochemical treatments for avoiding the anchorage, that is the initial stage in the layer formation. The proposed treatments deal with the decreasing of shear stress between the pellet and the refractory surface by means of closing the pores and eliminate sharp edges. The success of the treatments with sand and SAB for avoiding the anchorage is other factor that confirms the mechanism proposed. It is important to make clear that the time for testing in the rotatory cell was 30 min, but in some cases 10 min were enough for wearing the pellet. However, in order to be sure, these treatments were applied to specimens in the laboratory, in the pilot plant and finally in the industrial plant with a high degree of success (none layer formation).

5.3. Regarding with the model

Once again, in this experiments we tested the conclusions obtained in the seek for the mechanism. Indeed if the time, stress and temperature are enough for describing the major part of the mechanism, they explain by themselves their importance over the phenomena. The parameter of energy in the exponential therm [Eq. (1)] describes a phenomena that is not high dependent of the temperature as a chemical reaction usually is. This value is rather small, implying a physical process at atomic scale. The value of the exponential is in good agreement with Nagao [21–24] for contact with plastic deformation between particles, confirming once again what we already explained.

6. Conclusions

It was possible to reproduce layer formation at laboratory scale thanks to the design of rotatory cell that permitted to applied shear stresses in the pellet-refractory interphase, with material renovation as the degradation demands. It was demonstrated that the shear stress is the origin of the layer formation at laboratory scale. This explains one of the ways of the adhesion mechanism by anchorage between iron particles and refractory wall. The anchorage mechanism that is described in the reviewed literature is applied to fibrous materials or particles that can be holding together due to their shape, while the mechanism for the anchorage and growth explained here is not described in the reviewed literature. What we described here is a mechanism of several stages, powder generation with the adequate stress level for penetrating through the pores (material extrusion), sintered of these powders inside the pores, adhesion by sintering and plastic flow for having layer growth. It was tested at laboratory scale that adhesion between DRI and refractory could be avoided by means of a surface treatment with silica sand. The treatment is based on the decreasing of the porosity of the brick surface by means of the smelting of the surface itself or, according to the particular treatment, the power of silica sand as an added material with a torch of acetylene at temperatures above the 1700°C. The smelting of the more active parts on the surface such as edges and cracks or the fill of them with the material made a smother surface. With these actions we achieved two goals, the first one is to decrease the shear stress while the second one is to close the pores where the anchorage mechanism takes place. This procedure was developed and tested at industrial level; at the moment more than 6000 bricks have been treated for two different reactors with great success.

We also have an equation for describing the layer growth as a function of stress, time and temperature. Statistical methods confirmed that the proposed variables applied to the model are describing the process. From a physical and chemical point of view the equation form and the parameter values are in good agreement with models that describe plastic flow of materials under stress and high temperature conditions.

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