DEVELOPMENT OF LABORATORY TESTS TO EVALUATE THE REACTIVITY IN SPONGE IRON[1]

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Abstract

Sponge iron (DRI) is the product obtained in the direct reduction process, which is used as feedstock for the steel production by electric arc furnaces (EAF). DRI quality is defined by several parameters; one of the most important is the metallization degree (ratio of metallic Fe and total Fe). This ratio must be preserved until its use, so it is very important to prevent reoxidation. Reoxidation is a highly exothermic reaction, which under certain conditions it could get out of control to result in a violent reoxidation which leads to waste the material stored. Reoxidation will depend on the reduction process conditions, the storage conditions of the DRI and the characteristics of the iron ore used for its production. The latter is the main inconvenient and in some cases it has been the reason to stop using certain mines. This paper describes the operating problems caused by the violent reoxidation of the DRI and a methodology: Reactivity test, tuned up in IAS, to assess the oxygen avidity of the DRI. The results of this test will allow to estimate beforehand the behavior of recently obtained DRI, with the aim of adopting operative practices to preserve the DRI quality.

Key words: Reactivity; Direct reduction iron; Direct reduction; Midrex.

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1 INTRODUCTION

Information about the behavior that the reduced material may have during storage is useful for planning the handling. TenarisSiderca reduction plant did not have a technique to evaluate the reactivity of sponge iron. As some isolated events from violent reoxidation of the stored material have occured, TenarisSiderca decided to work together with IAS in developing a test aimed to predict the reactivity of the DRI. The test is designed based on a Midrex technique, which involves measurement of oxygen consumed by a small material sample of known mass at 50°C.

Initially numerous trials were carried out allowing to develop the methodology by modifying different parameters. This permitted us to obtain representative results of the behavior observed in plant. Later, trials were successfully conducted on samples from different suppliers.

Currently, this test is used to confirm the reactivity of certain shipments at plant showing certain signs of violent reoxidation.

1.1 Factors Affecting the Reactivity of DRI

Many factors contribute to these differences in reactivity or avidity for oxygen, but certainly the most influential is the morphology of the material, i.e. its porosity. Pellets are porous and more than half the pellet volume is air in the pore volume between iron grains, therefore, the surface area is high. For this reason, the DRI has a great tendency to reoxidize rapidly.

Other factors affecting reactivity are: the temperature reached in the reduction process, the source of iron ore, the time since the DRI was produced, DRI temperature and storage conditions:

- the reduction temperature has a great influence on the iron grain size and consequently on the reduced surface area of the pellet. At higher temperatures, the softening and melting of some grains are favored and pores become larger and occur in smaller amounts. Thus, the surface area decreases and consequently the reactivity.
- the mineral source is associated with the ore mineralogy, specifically to the grain structure. Different structures present different reactivities.
- the reactivity decreases as the time increases since the DRI was produced.
- the greatest effect occurs as soon as the DRI is exposed to an oxidizing environment. Then, the formation of an oxide layer on the surface of the iron inhibits further oxidation. The magnitude of this effect can be very large.
- the reactivity increases when the temperature of the reduced material is higher.
- the temporary storage of the DRI in an inerted atmosphere (eg a hopper) can decrease the tendency to reoxidation.
- the high content of dust in the DRI. Given its high specific surface, dust increases the risk of reoxidation.

1.2 DRI in Plant

1.2.1 DRI handling and storage

There are several alternatives to store sponge iron in TenarisSiderca. First, the material can be discharged to ground by two different sites: one located at the entrance of the Sponge Iron inerted hopper, the other before the final dispatch to the Steel mill. Moreover, the product can be lowered to floor and stockpiled in two ways. The first one is the formation of piles in sheds or warehouses, where the material is dry and protected from soil moisture, and the second one is the formation of stacks in the open air. These stacks are covered with canvas counterbalance to keep the material isolated from the rain. This method is more vulnerable to the reoxidation of the DRI as rain water can seep sometimes between the overlaps of canvas, and also soil moisture may also reach the material. Due to the high level of stock the storage capability is usually exceeded. At its maximum, approximately 70% of sponge iron is stored in piles outdoors.

Figure 1. DRI storage: warehouse.

Figure 2. DRI storage: outdoor pile.

1.2.2 Violent reoxidation in storage and handling

The way in which the material is stockpiled influences its tendency to violent reoxidation if this presents high reactivity. On one hand, the site chosen to discharge the material to the ground makes a difference. The material downloaded from the site before the hopper that contains DRI material, has not passed through the sieve, so it has an important content of fines (particles <6 mm, about 3%). The presence of reduced material powder represents a greater risk of reoxidation, since smaller particles have more surface area, and therefore more likely to react. In order to avoid this, the DRI material, already sieved, is normally discharged to the floor before the final dispatch to the Steel mill. However, before operational eventuality, it may be necessary to use the other site, so that the stored material will have a greater risk of violent reoxidation.

A material presenting high reactivity is prone to generate hot spots by reoxidation. Since this reaction is exothermic, the surrounding material undergoes a temperature rise which in turn promotes its own reoxidation. If this is not forewarned, this phenomenon leads to a violent reoxidation of the whole stored material. The release of heat and hydrogen formation generates a combustion that increases the temperature, causing the adhesion of the material by melting. Besides the risks associated with security, this means the total loss of DRI affected.

Additionally, the reactive DRI powder tends to generate burning points in the transportation system in areas where fines accumulation takes place. This can cause damage to the conveyor and structures, and if the material is stored, the powder can promote an ignition source for combustion initiation.

Figure 3. DRI burning in warehouse.

Figure 4. DRI burning outdoors.

The image on the left it can be observed a sponge iron burning point within a warehouse, generated by the ignition of powder accumulated in a column and in contact with an air stream. The spread of the reoxidation is evidenced by the darker color of the material. The image on the right shows the same phenomenon in a pile outdoors.

A factor which significantly increases the reactivity of the iron sponge is the temperature of the reducing gases used during the reduction and the bed temperature of the material in the area of bustle. With the appearance of the coating and injection of oxygen, which allowed the use of reducing gases at about 950 to 980ºC, the reactivity of iron sponge significantly decreased.

Beyond the above, it should be noted that there are iron ore and pellets produced with these minerals, which by their morphology, have a high reactivity and tendency to violent reoxidation. These materials should always be maintained under an inerted atmosphere or low content oxygen, and sent to be processed at the steel mill, as quickly as possible. The storage of these involves a high risk.

The reactivity test should identify and alert when an iron ore with high tendency to violent reoxidation will be used, so that the necessary precautions could be taken in order to prevent the DRI ignition.

2 MATERIALS AND METHODS

This technique, based on Midrex methodology was tuning in IAS to assess the reactivity of sponge iron in different samples. The following describes the reactor used, the samples and the sampling and the procedure for performing the test:

2.1 Reactor and Auxiliary Equipment

Figure 5 shows the reactor used to determine reactivity. It was built following the Midrex instructions.

It is a stainless steel container (1), with seal and two inputs for the N2 gas flow and the air injection (3). An electric resistance surrounds the reactor for its heating (2). An air dryer is also attached (4), a coil for heating the injected air (5) and a U-tube manometer (6).

During the heating step, N2 enters through the bottom input, keeping the upper input open to allow gas flow.

Then, the air injection stage continues. The connection and flow is similar, preheated air entering at 50°C through the bottom input of the reactor.

After the injection of air, the monometer is connected to the upper input and the measurement of pressure is followed, which indicates the consumption of O2 in the reactor.

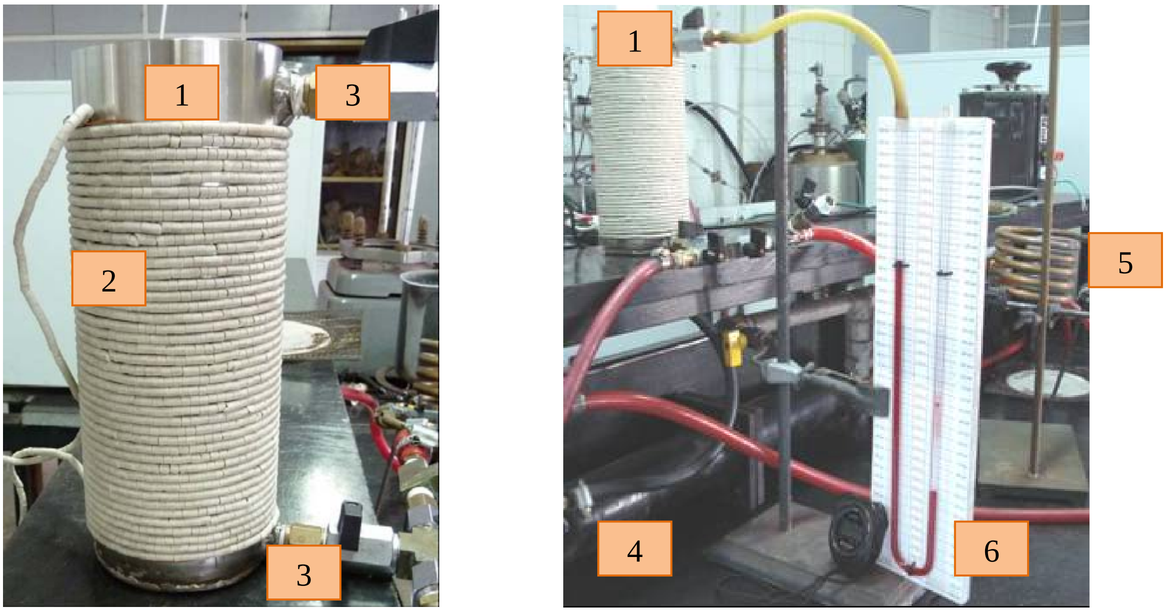

Figure 5: Reactor for determination of reactivity(right) and complete equipment(left).

2.2 Samples

The samples used for this study come from basket tests carried out direct reduction furnace of Tenaris Siderca.

This test enables to obtain reduced material from iron ores that are desired to be tested, subjecting them to actual conditions in the reducing furnace.

The technique involves placing iron ore in wire mesh cylinder and introducing the baskets in the reducing furnace. The basket crosses the bed of the furnace and the iron ore passes through all the stages corresponding to the reduction process. Finally, the basket is recovered in the discharge of the furnace and sponge iron therein is analyzed.

Two different iron ores, one used as reference and the other to be tested, are usually included in the same basket. From the obtained reduced material, different comparisons can be made regarding the quality, particle size, and even further tests such as reactivity.

When the basket is used to reduce material whose reactivity is measured, it must be recovered as soon as possible to place the DRI into an inerted container with nitrogen to stop the initial reoxidation and to assess the reactivity in a representative manner.

The following pictures show three stages of the basket test: preparation, inlet furnace and recovery.

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Figure 6: Basket set up.

Figure 7: Reduction furnace inlet tube for baskets.

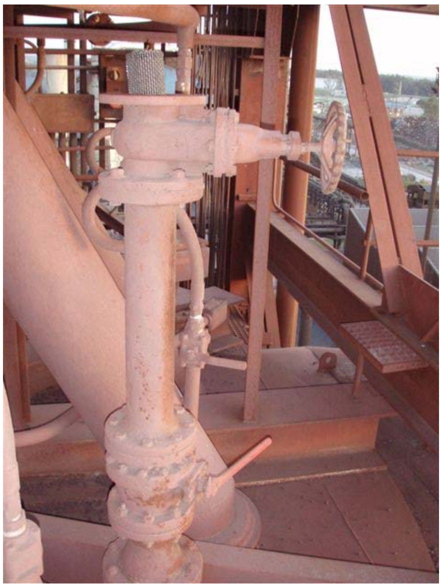

Figure 8: Deflector grill at reduction furnace discharge.

The first samples studied were not inertised. Then it was adopted as a routine to put the samples in N2 atmosphere to prevent passivation of the material in the presence of O2, which increases as time passes. The effect of this passivation is revealed in the results of tests conducted on the same sample, with and without inerting. Three different suppliers were studied: A, B and C. The numbers next to the letters indicate different samples. Thus, nine samples of the supplier A (from A1 to A9), one sample of B (B1) and two samples of C (C1 and C2) were tested.

2.3 Procedure

The procedure is based on the Midrex technique. It consists of the following steps:

- approximately 1.3 kg sample of sponge iron is placed within a preheated reactor. The reactor is closed so as to be airtight.
- reactor + sample is heated altogether, via the resistance located on the surface of the reactor to reach 50°C inside the reactor. During the heating, N_2 is circulated to prevent reoxidation of the sample.
- the reactor is purged with air at 20 l/min for 30 seconds. This air before entering the reactor, passes through a dryer to remove moisture and a heated coil with direct flame that heats the air to 50°C.

- then the reactor is connected to the U-tube manometer and the pressure is recorded periodically. U-tube manometer readings are plotted versus time and the points are adjusted with a line. From here a slope is obtained: (D-E) / (F-G) to replace in the final formula.
- Reactivity is calculated as:

$$R = \frac{(A - B) \times (D - E)}{C \times (F - G)} \times \frac{1.440.000}{P_{test} \times 1000} \times \frac{273}{(273 + T)} \frac{[Nm^3]}{[tn \times day]}$$

Where:

- R = Reactivity (Nm^3 O_2 consumed / t of dry material per day)
- A = Weight of water plus sample, item 7. (g)
- B = Weight of wet sample, Item 8. (g)
- C = Weight of dry sample, Item 1. (g)
- (DE) / (FG) = Slope of the linear fit: P vs. time.
- T = temperature at which the test is performed, 50°C.
- P_{test} =
- Atmosphere pressure (mmH_2O)

- Expression of results:
  Reactivity is calculated at 5, 20, 60 and 90 minutes during the test, using the formula in item 5.
  If at the beginning of the test, the variation of P is void or decreases as time passes by, these values are ignored for the calculation of the slope.

3 RESULTS AND DISCUSSION

First we analyze the non inerted samples and then the inertized ones. Results are compared to analyze the different behaviors. The strong influence of air exposure on the values of reactivity is also evaluated.

3.1 Non Inerted Samples

The samples studied: A1, B1 and C1, have very different behavior. Figure 9 shows the oxygen consumption vs time during the test.

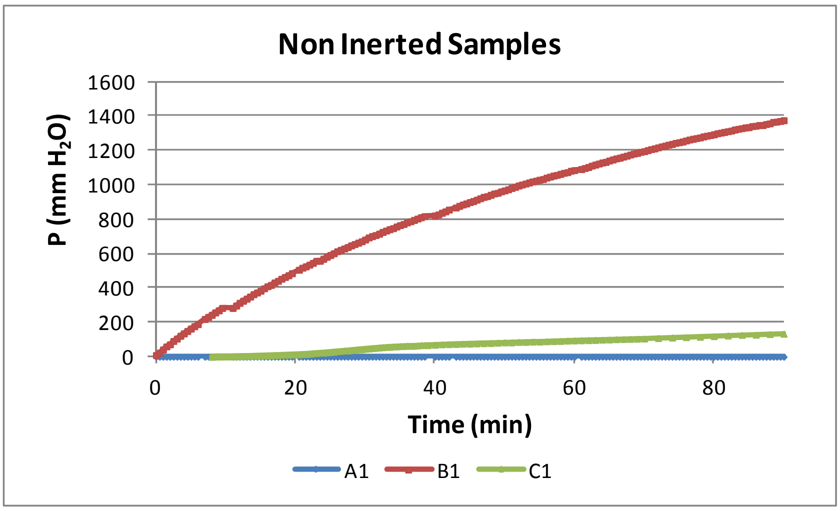

Figure 9. Results, non-inerted samples.

The slopes of these lines provide us the rate of consumption of O_2 and will be used for the calculation of reactivity.

Table 2 summarizes the results of reactivity at 5, 20, 60 and 90 minutes during test.

Table 2. Results, non-inerted samples

	Reactivity (Nm^3 O_2 / tn. day)			
	5 min	**20 min**	**60 min**	**90 min**
A1	0	0	0	0
B1	1,445	1,082	0,804	0,668
C1	0	0,062	0,119	0,099

3.2 Inerted Samples

After basket test, the sample was placed in a closed vessel and immediately inertized with 100% N2 to avoid passivation of the material in the presence of O2.

Samples studied presented different behaviors. The figure 10 shows the oxygen consumption vs time during the test.

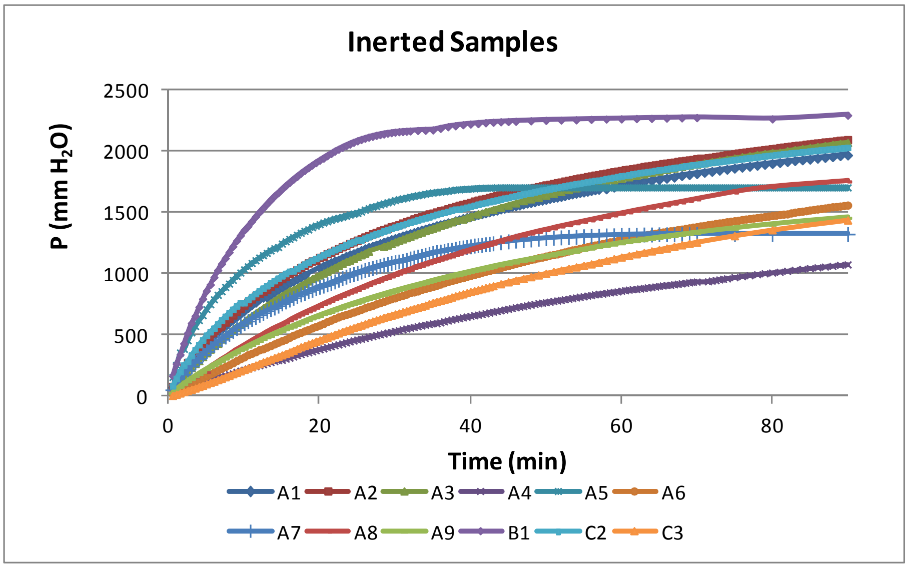

Figure 10. Results, inerted samples.

Table 3 summarizes the results of the studied samples.

Table 3. Results, Inerted samples

	Reactivity (Nm^3 O$_2$/tn. day)			
	5 min	**20 min**	**60 min**	**90 min**
A1	3,4997	2,1548	1,6740	0,8185
A2	3,5223	2,2691	1,1322	0,8074
A3	2,9509	2,0280	1,1910	0,8900
A4	0,9861	0,8050	0,6140	0,5200
A5	3,9614	1,9270	0,6260	0,3220
A6	1,1290	0,9907	0,7119	0,5671
A7	2,2652	1,3371	0,6483	0,4899
A8	1,3403	1,2164	0,8216	0,7120
A9	1,4024	1,0361	0,6527	0,5602
B1	7,0548	3,9512	1,4638	1,0290
C1	4,1237	2,3181	1,1109	0,7921
C2	0,7041	0,8013	0,6725	0,6085

If we analyze the results we observe different behaviors regarding the reoxidation of sponge iron.

The non inerted samples presented very different behaviors. The three studied pellets come from different suppliers, which differ in their morphological characteristics and origin of iron ore from which the pellet was produced. These factors influence the reactivity results. Sample A1 did not show any P change, sample B1 was the most reactive and sample C1 presented a very low reactivity. See Figure 11.

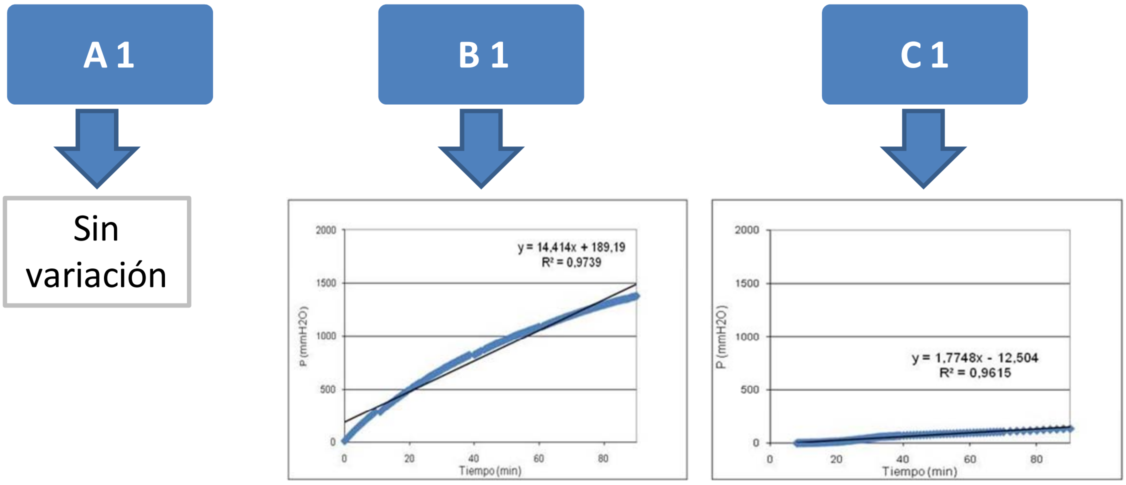

Figure 11: Results: Non Inerted Samples.

Inerted and non inerted results of Samples A1 and B1 were compared. The inerted samples presented much higher reactivity. This is because the formation of the oxide layer in oxidizing atmosphere has been inhibited by the nitrogen used for the storage of the sample. The samples show the same trend, sample B1 is much more reactive than sample A1. Figure 12.

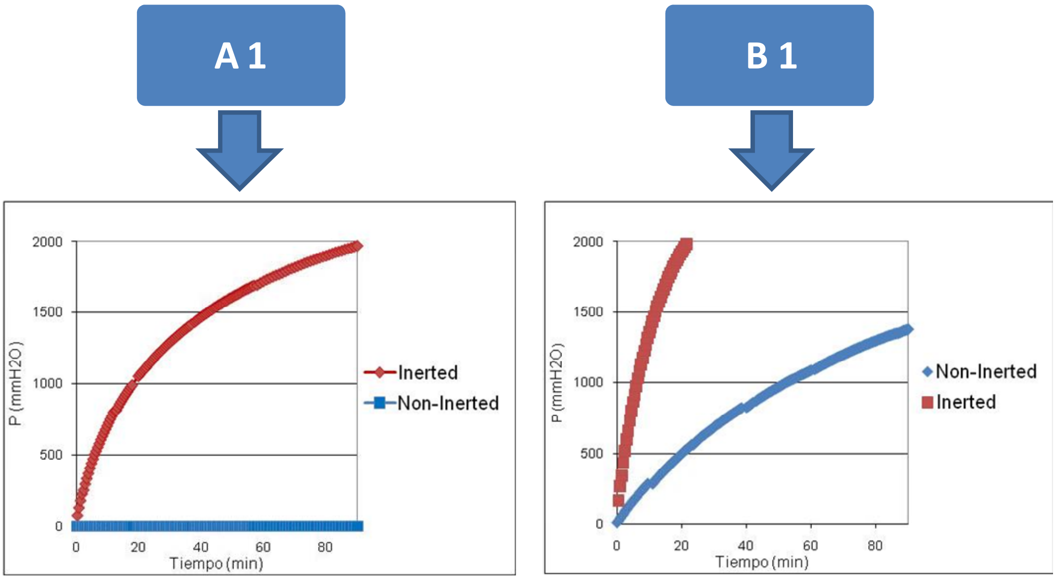

Figure 12: Results: Inerted and non-inerted samples.

Comparing the inerted samples, sample B is the most reactive, followed by sample C, and then samples A. Figure 13.

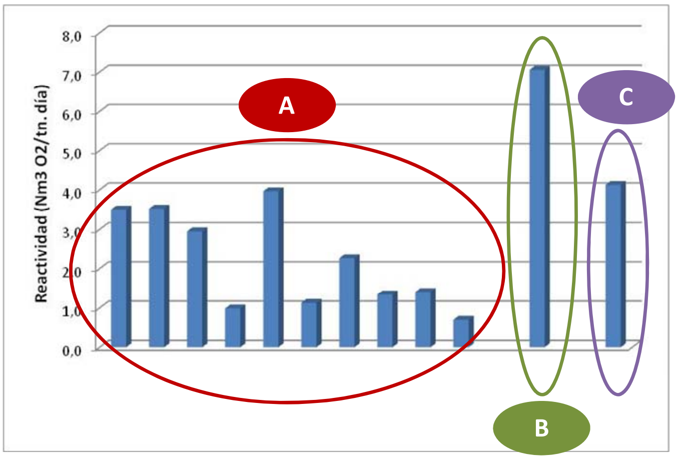

Figure 13: Results: Different Suppliers.

Samples A which belong to the same supplier present different behaviors. Some samples show a continuous and important oxygen consumption. In other samples the consumption is continuous and mild. The remaining samples present a great initial consumption, reaching a certain point when the oxygen consumption finishes and the pressure remains constant. Figure 14.

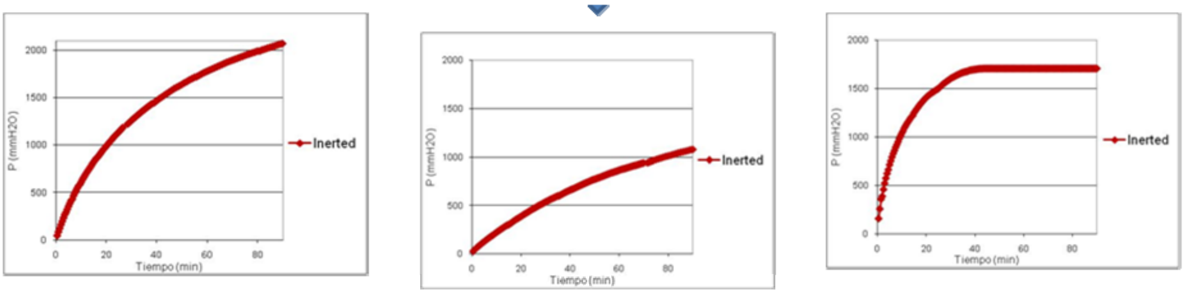

Figure 14: Results: Different Behaviors.

4 CONCLUSIONS

- The Midrex technique was successfully adapted. The test allows to obtain a reactivity predictive value of the DRI showing correlation with the behavior in plant.
- It was found that the inerting of the samples is key to obtain representative results.
- There were differences in the reactivity of the samples from different suppliers and even between different samples of the same supplier.
- Continued testing will increase the amount of data available, thus strengthening the relationship between results and the observed reactivity at industrial scale.

REFERENCES

1 R, L. HUNTER; “Handling and shipping of DRI/HBI”; Direct Reduced Iron, p. 121-125, 1999.
2 Reactivity Test. Midrex Direct Reduction Corporation.