SELF REDUCED IRON ORE PELLETS USING FLEXICOKE AS REDUCTANT

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INTRODUCTION:

The use of flexicoque as a replacement of higher valued raw materials, has been considered, since the implamentetion of flexicoking technologies for upgrading heavy Venezuelan crude oil would increase the production of this by product.

One of the most promissing alternatives is to use this material as reductant of iron ore, because of the large amount of this mineral in Venezuela and the high demand of reduced iron for steel production.

This work is concerned with the use of flexicoke as solid reducing agent for producing direct reduced iron ore in pellet form and with the evaluation of the product obtained by the fusion of these reduced pellets.

REDUCTION OF IRON ORE USING SOLID REDUCING AGENT:

The direct reduction of iron oxides by carbon has been extensively investigated in recent years. The work done has demonstrated that such process occurs via the gaseous intermediates CO and CO_2. Initially the carbon monoxide is produced by a reaction of carbon with oxygen from the oxide in contact with the carbonaceous materials. This carbon monoxide reduces the oxides, producing carbon dioxide which reacts with carbon to form more CO; thus restoring the reducing potential of the gas phase that allows the reduction to continue. According to Baldwing [1], the chemical reactions associated with the process are as follows:

$$3Fe_2O_{3(s)} + C_{(s)} = 2Fe_3O_{4(s)} + CO_{(g)} \quad (1)$$

$$Fe_3O_{4(s)} + CO_{(g)} = 3FeO_{(s)} + CO_{2(g)} \quad (2)$$

$$FeO_{(s)} + CO_{(g)} = Fe_{(s)} + CO_{2(g)} \quad (3)$$

$$CO_{2(g)} + C_{(s)} = 2CO_{(g)} \text{ Bouduard reaction} \quad (4)$$

Previous investigation work related with the reduction of iron oxide with carbonaceous materials: charcoal, carbon, graphite, lignite coke [2, 3, 4, 5, 6, 7 and 8] have reported that the variables of major influence on this type of reduction process are: temperature, carbon content and reactivity of the carbonaceous materials. Also they demonstrated that the rate of reduction, increases with: increasing reduction temperature, increasing carbon percentage and decreasing particle size.

PRODUCTION OF COLD BOND SELF REDUCING PELLETS (SR-PELLETS):

SR-pellets are produced when carbon is incorporated in the mixture with iron ore and binders. Then an internal solid-solid reduction occurs according to the following general reactions [9].

$$Fe_2O_3 + 3C \rightarrow 2Fe^\circ + 3CO \quad (5)$$

$$Fe_2O_3 + 3CO \rightarrow 2Fe^\circ + 3CO_2 \text{ (secondary reaction)} \quad (6)$$

Fig. 1, illustrates the different mechanisms involved in the reduction of a self-reducing pellet and a conventional one reduced with external carbon [9]. Here it can be seen that the rate and percentage completion of reduction, is higher for the self-reducing pellet than for the conventional pellets with external carbon.

Fig. 2 shows schematically the different steps for producing self-reduction pellets (SR-pellets). The self-reduced pellets can not be hardened thermally, because the reduction process would occur before the temperature for pellet induration is achieved (conventionally, ∿ 1300°C), since reduction reactions of iron ore by carbon may start at temperatures higher than 600°C. Therefore, SR-pellets must be produced by other pellet hardening processes i.e without firing. Such processes are designated as cold bond pelletizing.

The binders in the cold bond processes play an important role, because they must have the ability to improve green ball formation as well as the mechanical properties of green, dry, and indurated pellets [9]. Four types of binders are evaluated in this work; Portland cement, $Ca(OH)_2$, a cellulose base binder called Peridur [13] and SiO_2 (clay).

EXPERIMENTS

Methodology used

The experimental procedure is shown schematically in Fig. 3.

The reductibility of the iron oxide in the presence of flexicoke, was determined experimentally by using a thermogravimetric set up (continuous tests) and the tubular furnace (discontinuous tests) as shown in Figs. 4 (a) and (b), respectively. The removal of oxygen was measured by the loss in weight of the sample, this is known as the Loosing - weight method. By plotting the percentage loss in weight or the lost weight fraction versus time, a measure of the of the reducibility can be obtained.

For the evaluation of flexicoke as a solid reducing agent of iron ore and for determining the optimum mixture for manufacturing SR-pellets, briquettes of 10 mm in diametter and 5 mm height, were prepared by using a compressive strength of 2700 kg/cm². Two parameters were considered in the reduction of the samples, flexicoke percentage and its particle size. The experiments were performed at the same temperature (1050°C). This temperature was selected, since it was found high conversion rate at this temperature when reacting it with CO_2 [12]. Fifteen mixtures of iron ore plus flexicoke were tested, with three types of binders: hydrated lime, peridur and clay. Portland cement was evaluated as binder by making SR-pellets of iron ore and flexicoke [10]. Once was the optimum mixture determined, the effect of temperature on the reduction processes was analysed. Each experiment was run out three times for checking results reproducibility.

The SR-pellets reduction experiments were carried out using an inert atmosphere (argon), and five different temperatures: 950°C, 1000°C, 1050°C, 1100°C and 1150°C. The fraction of weight lost of the reduced samples were determined as a function of the maximum weight loss, in order to compare the behaviour of the pellets reduced at these different temperatures.

The remnant carbon content after reduction was determined by a carbon and sulphur analyser LECO. A qualitative analysis of reduction products, was carried out by X-ray diffraction, using a difractometer PHILLPS, model 1840, with the following experimental conditions: 35kv, 20mA, 0,03 2θ seg with Ni filter. The metallic iron oxide phases present in the reduced products were determined by Mosbaüer spectroscopy. The values for metallic iron obtained by this technique were used to determine metallization percentage (%MET) according to the following relationship:

$$\%MET = [MFe^{\circ}/MFe_{tot}] \times 100 \quad (9)$$

Where: %MET = percentage of metallization.
MFe° = iron mass.
MFe_{tot} = total iron mass as obtained by chemical analysis.

The mechanical compressive strength (crushing strength) of self-reduced pellets was determined by using a universal mechanical test equipment INSTRON of 500 kg capacity. The fracture surface of reduced products was also observed using a scanning electron microscope (SEM): PHILLIPS model 505. Attached to it a X-ray energy dispersive system (EDAX) and a wave length spectrometer of X-ray (WDAX) for qualitative and semiquantitative analysis.

The characteristics of the raw material used in the present work are shown in Table 1.

RESULTS AND DISCUSSION

FLEXICOKE AS IRON ORE REDUCTANT:

It was found that flexicoke acts as solid reducing agent of iron ore and the reduction rate increases with flexicoke content up to 17% (see Fig. 5). The curve shape indicates that there is an initial high rate of weight lost, and 15 to 30 minutes after the test started the slope of the curve tends to cero. The initial stage of the curve is related to loss of the water contained in the SR-pellets, the pirolysis of the volatile materials present in the flexicoke and the reduction of hematite to magnetite and magnetite to wustite by $CO_{(g)}$ generated by the flexicoke gasification, according to Bouduard reaction (4). The second stage of the curve is related to the reduction of wustite to iron. Fig. 6 (a) shows the effect of reduction temperature on the reduction of iron ore, from these curves it can be observed that the higher the reduction temperature, the higher the fraction of weight lost, and hence, the higher the reducibility. Fig. 6(b) shows the effect of reduction temperature on the presence of magnetite, wustite and iron. Also it was found that decreasing flexicoke particle size, increases reduction rate.

MANUFACTURE AND EVALUATION OF COLD BOND SELF REDUCING PELLETS (SR-PELLETS):

Table 2 shows the mixtures used for SR-pellets manufacturing, and also pellets quality before and after reduction tests at 1150°C for 90 minutes. Here it can be observed that the SR pellet manufactured with cement as a binder showed the highest strength 20,4 kg/pellet, although this value is lower than the required for the thermally indurated pellets (320 kg/pellets). The reduced SR pellets showed cracks, peeled surface, double structure (layer-core), and the mechanical strength decreased in 82%.

On the other hand, the SR-pellets with $Ca(OH)_2$, as a binder, showed an increment of 214% in mechanical strength after reduction. Although thes value obtained: 40 kg/pellet, is lower than the required by steel making industry for reduced pellets (60 kg/pellet).

Peridur and SiO_2 binders were used to evaluate the possibility of improving mechanical strength, however no improvements were noted when using them. Therefore the evaluation was focused on SR-pellets with cement and $Ca(OH)_2$ as binders.

The highest percentage of metalization was obtained for the SR-pellets with $Ca(OH)_2$ as binder.

STRUCTURAL CHANGES OBSERVED IN SELF REDUCED PELLETS:

The fractured area of SR-pellets with cement, as binder, reduced at 950, 1000, 1100 and 1150°C showed an internal structure of interconected pores giving a "sponge" like appearance, which indicated high degree of particle decohesion.

Whiskers or fibers of iron emerging from the oxide phases were present (see Fig. 7). The iron fibrous growth tended to be favored in the areas of oxide phases close to flexicoke particles, similar results were reported by Seaton, et al. [8]. When using charcoal as iron ore reducing agent. Internal fusion was also observed (see b in same figure), which may have occurred when the carbon was transferred from the gaseous phase to the reduced iron, producing an eutectic which fusion point is close to 1000°C [11].

Similar morphology was observed in the fractured area of SR-pellets with $Ca(OH)_2$ as binder, when they were reduced at 950 and 1000°C (see Fig. 8a). This phenomena could be accounted for by a low rate in the reaction of carbon gasification (4) and combined with a decrease in the wustite activity by the presence of calcium oxide, inhibiting iron nucleation [8].

The scanning photomicrograph of the SR-pellet with $Ca(OH)_2$, reduced at 1100°C (see Fig. 8b) showed isolated porous in a continuous matrix, indicating a more compact structure (compare with Fig. 8a).

Table 3, indicates, the volumen contraction of pellets containing $Ca(OH)_2$ as binder and the incidence of whiskers. Here it can be observed that the presence of whiskers is associated with either swelling or low volume contraction of the reduced pellets, and that these whiskers tend to dissappear as the massive iron sinterization takes place at longer periods of residence time, and at higher reduction temperatures. Also, from here can be inferred that the strengthening mechanism of SR-pellets is the massive iron sinterization during reduction. If this process does not occur the reduced pellet is highly porous and easily disintegrable, which was the case of the SR pellets with cement as a binder. The lack of massive iron sinterization is associated with the high amount of coarse remnant flexicoke particles, and to phases rich in calcium (from the high percentage of cement used as a binder) which act as barriers for iron nucleation. This lead to iron whiskers growth which are unable to sinterize each with other, promoting swelling and cracks in the reduced pellets.

FUSION TESTS RESULTS:

Table 4 shows the metallic charge patterns used for performing the fusion tests in the induction furnace, and the chemical analysis of the fusion products. If fusion 1 and 2 are compared, it can be seen that the product obtained from fusion 1, contains the double amount of carbon, vanadium and sulphur with respect to fusion 2. This is due to the fact that the remnant carbon content in SR-pellets with cement, is larger, and also that in the manufacture of these pellets a combination of two types of flexicoke (low and high vanadium content) were used.

In general, a relative high carbon and vanadium content could be acceptable, depending on the final use of the pellets, for example: as raw material for foundry (grey iron) or alloyed steels of high carbon content, providing the use of a desulphurizer during fusion process.

The fusions 3 to 7 were performed using only SR-pellets containing $Ca(OH)_2$ as binder. It can be observed that the amount of carbon and sulphur, increase with the amount of pellets in the metallic charge, except in fusion 7, where the volume of slag generated did not allow good interaction of the added pellets with the liquid phase.

Fig. 9, shows the optical photomicrographs indicating the microstructure of the fusion products, Fig. 9(a) corresponds to fusion 1, the light areas correspond to ferrite which are distributed along boundaries of very coarse prior austenite grains, and as plates within the grains; the matrix is fine perlite, a morphology characteristic of medium carbon steels. Fig. 9(b) corresponds to fusion 2 where can be observed widmanstatten patterns of proeutectoid ferrite in a matrix consisting of ferrite and fine perlite. This type of microstructure is characteristic of low carbon steels.

CONCLUSIONS:

The results of this investigation lead to the following conclusions:

- Flexicoke acts as solid reducing agent of iron ore and is effective at temperature >1100 °C.

- It is possible to agglomerate the iron ore with flexicoke by using cement, $Ca(OH)_2$, clay and peridur as binders, and manufacture cold bond self reducing pellets. The hardening mechanism is the massive iron sinterization during reduction, however these pellets do not fulfill the minimum value required for conventional pellets mechanical properties, because of the lack of a stable skeleton for binding together all the particles and the sufficient strength to support handling and transportation conditions prior to reduction; as well as sufficient compressive strength to overcome the pressure of conventional metallurgical reactors (rotary kiln or shaft type) during reduction process.

- Self reduced pellets with flexicoke as iron oxide reductant can be used as raw material for producing gray iron, or carbon steels.

RECOMENDATIONS:

An alternative for the reduction of SR-pellets with flexicoke, would be the rotary grid or a rotary open hearth furnace under isothermal conditions with high heating rates that warranties no temperature gradient in the pellets. Under these circunstances the SR-pellets residence time, in the low temperature zones would be disminished and the problems of disintigration by abrasion would be overcome. Fig. 10 shows schematically the suggested process for reducing SR-pellets. But further investigation is requiered to determine optimun operational conditions.

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12. SEATON, C.; SPECHT, M. I.; ESTELLER, D.; CONTRERAS, G. and MORALES, A. "Potential Uses of Flexicoke in the Venezuelan Steel Industry", Iron Making Conference Proceedings, 1989.
13. From Dreeland Colloids Inc., 1670 Broadway Suite 3335, Denver, Colorado.

Table 1. Characteristics of the raw material used (weight).

Analysis	Flexicoke (Bed)	Flexicoke (Filter)	Iron ore		Binders (*) Cement Portland		Binders (*) Hydroted lime	
Fixed C	88,4	39,22						
			Fe_2O_3	94,33	CaO	64,0	CaO	70,00
			Al_2O_3	0,64	SiO_2	20,0	MgO	0,90
S	2,4	2,3						
			P	0,065	Al_2O_3	5,0	A_2O_3	0,60
V	1,34	16,22	S	<0,03				
					TiO_2	0,3	SiO_2	1,10
Ni	0,39	0,46	SiO_2	1,24				
					P_2O_5	0,1	Fe_{tot}	0,10
Volatile material	3,1	11,6	Fe_{tot}	64,3				
					Fe_2O_3	2,5		
As h	4,1	30,2			Mn_2O_3	0,1		
					MgO	1,5		
High Heating value (Cal/gr)	7305	5265						
					Na_2O	0,2		
					K_2O	0,9		

(*) Peridur is a cellulose base binder (13)
Clay was from Guárico Mines (Venezuela)

Table 2. Mixture patterns for manufacturing SR-pellets (weight %):

Binders	13,2 cement	2,0 $Ca(OH)_2$	0,08 Peridur	0,9 SiO_2
Iron ore	65,8	80,77	82,43	81,67
Flexicoke	5,3 (bed)	17,23 (bed)	17,49 (bed)	17,34 (bed)
	15,8 (filter)	-	-	-
Hardening time	7 days	-	-	-
Crushing Strength (kg/pellet)	20,4	1,78	1,64	1,60
Reduction results: (argon atmosphere at 1150°C).				
% Fe°	96,9	82,94	49,82	36,16
% Metalization	75,9	89,90	55,17	45,90
% Remnant Carbon	9,7	2,00	-	-
% FeO	13,0	6,27	26,02	11,45
Crushing strength (kg/pellet)	3,7	40	-	-

Table 3. Incidence of iron whiskers and volumen contraction percentage for reduced pellets containing $Ca(OH)_2$ as binder.

Reduction temperature (°C)	Residence time (min)	Presence of iron whiskers yes	no	Partial volume changes percentage
950	5	x		0.65
	60	x		-13.58
	90	x		3.56
1000	5	x		-7.22
	60	x		6.91
	90	x		13.34
1050	5	x		1.73
	60		x	25.69
	90		x	34.69
1100	5	x		-6.23
	60		x	27.82
	90		x	46.06
1150	5	x		-4.38
	60		x	50.68
	90		x	51.16

Table 4. Metallic charge patterns for fusion tests and chemical analysis of fusion products.

		Fusions 1 (*)	2 (**)	3 (**)	4 (**)	5 (**)	6 (**)	7 (**)
Metallic charge pattern	Self-reduced pellets (weight %)	13.1	13.1	15	15	30	30	45
	(g)	500	500	522	522	867	867	878
	Scrap (Steel SAE 1010) (g)	3316.2	3316.2	3048	3048	2036	2036	2968
Chemical composition of fusion products (Weight %)	Elements							
	C	0.51	0.25	0.60	0.37	0.64	0.53	0.03
	S	0.13	0.09	0.09	0.08	0.22	0.23	0.29
	Mn	0.20	0.12	0.29	0.16	0.14	0.20	0.05
	Ni	0.06	0.04	0.04	0.04	0.04	0.05	0.05
	Si	0.03	0.06	0.09	0.08	<0.01	0.05	<0.01
	V	0.15	0.03	0.04	0.05	0.08	0.08	0.04
	P	0.03	0.02	0.03	0.02	0.03	0.03	0.04

* Self-reduced pellets containing cement as binder
** Self-reduced pellets containing $Ca(OH)_2$ as binder.

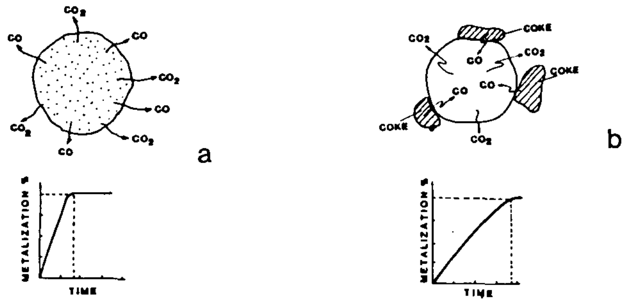


Fig. 1. (a) Self reducing pellet. Reaction (5) and (6) occurs internally.
(b) Conventional pellet with external carbon. Reaction (5) occurs at the pellet-carbon contact area and (6) inside the pellet by diffusion.

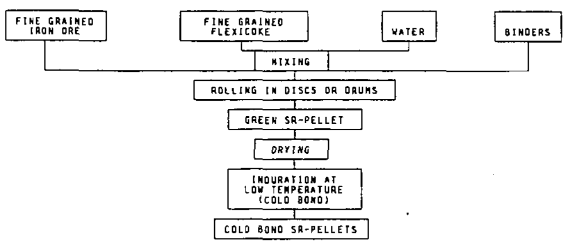


Fig. 2. Steps for producing cold bond self-reduced pellets.

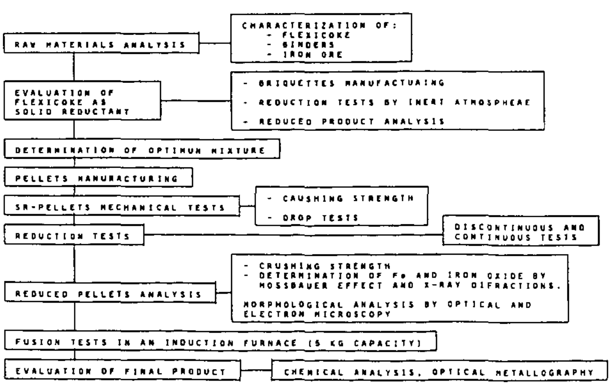


Fig. 3. Methodology used.

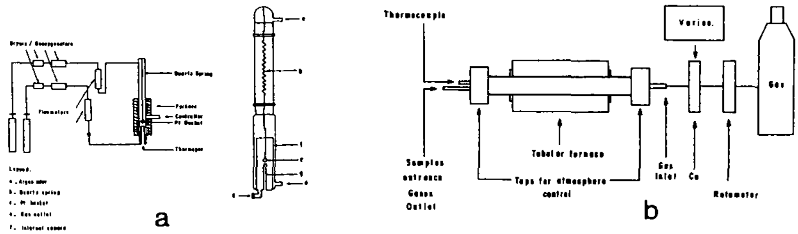


Fig. 4. (a) Thermogravimetric set up for continuous tests
(b) Tubular furnace for discontinuous tests.

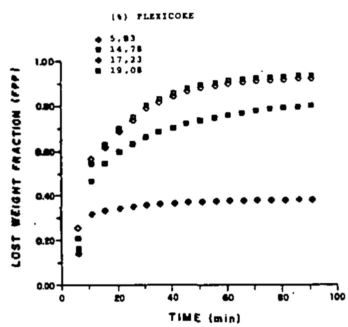
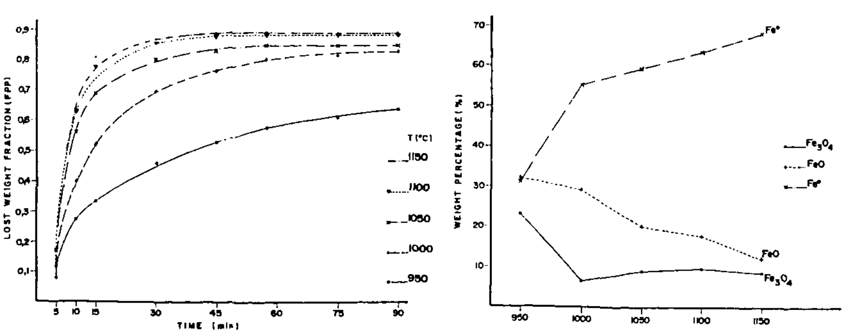


Fig. 5. Effect of flexicoke content in the reduction of iron ore.



(a) (b)

Fig. 6. Effect of temperature on (a) reduction rate (b) the presence of magnetite, wustite and iron.

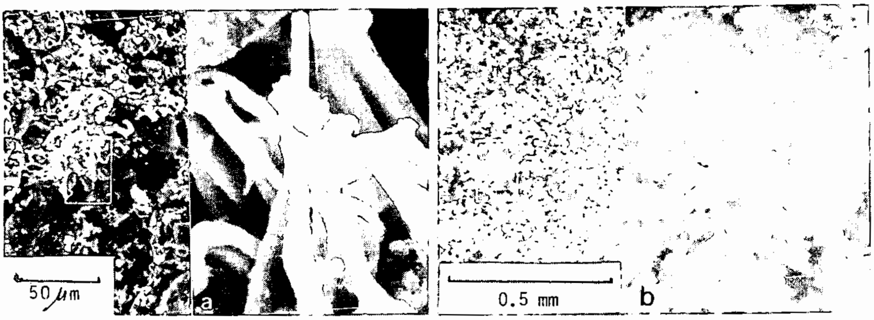


Fig. 7. (a) Scanning photomicrograph showing whiskers of iron, found in reduced pellets containing cement as a binder. (Reduction temp. 950°C).
(b) Scanning photomicrograph showing internal fusion when these pellets where reduced at 1150°C.

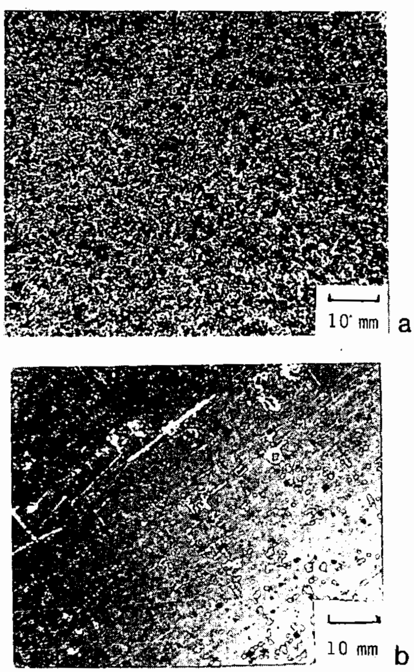


Fig. 8. SR-pellet containing $Ca(OH)_2$ as a binder. (a) reduction temp. 950°C (b) 1100°C.

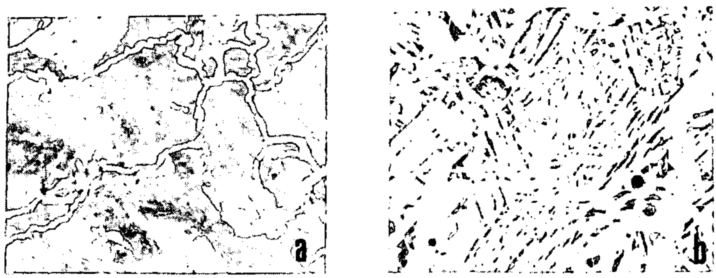


Fig. 9. (a) Optical photomicrograph of fusion 1 (100x).
(b) Optical photomicrograph of fusion 2 (100x).

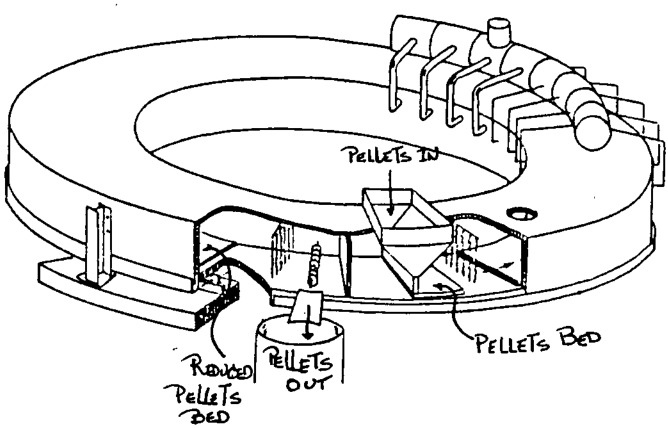


Fig. 10. Schematic view of a rotary open hearth furnace.