

Reduction of Iron Oxides in Solid Wastes Generated by Steelworks

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Abstract

Solid wastes generated by integrated iron and steel works cause environmental pollution and therefore must be discarded accordingly. Extensive research is being conducted for the recovery and elimination of the iron oxide that these wastes contain. The production of sponge iron from these wastes could be considered a method of beneficiation. In this study, the reduction of cold-bonded pellets produced from the solid wastes of Ereğli Integrated Iron and Steel Works (ERDEMİR), using different reducing agents, was investigated. A rotary furnace was utilized for this purpose and the effects of different reducing agents, the ratio of C_{fix} / Fe_{total} , temperature and time on the reduction were studied. The kinetics of the reduction process were also investigated and the data obtained were correlated with the Ginstling-Brounshtein model. The activation energy of the reduction was found to be 48.5 kJ/mol.

Key Words: Solid waste, Reduction, Iron oxides, Steel plants, Sponge iron, Recovery.

Introduction

The management of wastes generated by integrated steel works has become an important issue due to ever-tightening environmental regulations. Until the last decade, the slag, dust and sludge generated by integrated steel plants was called “waste”, but now this term has been replaced with “by-product” due to intensive re-utilization of these wastes. An integrated steel plant generates approximately 420 kg of solid waste per ton of steel produced, consisting mainly of slag, dust and sludge. Disposal and/or re-utilization of these wastes cost additional \$ 20/t steel to the manufacturer (Szekely, 1996). A major portion of the dust and sludge is reused in sintering plants, while some thermal treatment techniques have been developed for re-using the remaining portion, particularly from the gas cleaning systems of blast furnaces and basic oxygen furnaces. Sintering plants, apart from their primary function of agglomerating fine iron ore, have acquired an outstanding position in the flow of materials of an integrated steel plants for recycling wastes. The reuse of dust and sludge in sintering plants is restricted

due to the lowering of the particulate emission value to 50 mg/m³ by environmental regulations (Philipp & Endell, 1996). The oily mill scale could not be reused since it causes fires in the electrostatic filters. Table 1 lists several techniques developed for the re-utilization of ferriferrous dust, sludge and mill scale type wastes.

Reduction of iron oxide by carbonaceous materials is not only of industrial significance for the production of pig iron and sponge iron but is also of considerable theoretical interest. Consequently, a good deal of work on this subject has been reported in the literature (Rahman, Haque & Haque, 1995; Seatan, Foster & Velasco, 1993; Dutta & Ghosh, 1994; Dey, Biswanath & Basumallick, 1993; Bryk & Ku, 1986). In this study, the reduction behavior of cold-bonded composite pellets, produced from blast furnace slag and clinker, was investigated. The term “composite pellet” refers to a pellet that consists a mixture of iron oxide bearing fines and carbonaceous material (coal, coke, etc.) to which cold bonding techniques have imparted sufficient green strength for subsequent handling.

Table 1. Techniques developed for the beneficiating of solid wastes generated by the integrated iron and steel works.

Ore Preparation Techniques	Pyrometallurgical Techniques
Hydrocycloning of BF sludge	Inmetco®
Cold bonding agglomeration of dusts	Circulating fluidized bed
Electrochemical pretreatment of sludge	Romelt®
	De-oiling of oily mill scale by rotary tubular kiln
	Injection of oily mill scale to BF
	Carbofer®
	Hot briquetting of BOF filter dust
	Microwave treatment of oily mill scale

The raw material used in this study was a mixture of iron-oxide-containing solid wastes, prepared with respect to their formation ratios in the actual plant. This mixture contained 67% of the stoichiometrically required carbon coming from blast furnace dust and sludge. Thus, coke dust, produced in the coke plant of integrated steel works, was added to this charge and reduction tests were performed. The reduction behavior of the pellets was investigated from the viewpoints of both utilization of the cold bonded pellets in the blast furnace and in the sponge iron production.

Experimental

Raw materials

The chemical analysis of solid wastes generated

in ERDEMIR and the binders (clinker and BF slag) for the cold bonding agglomeration are shown in Table 2 with the yearly production values of wastes. Powders of coke and graphite were used in the experiments as reducing agents. The chemical analysis of these reducing agents is shown in Table 3.

Experimental Procedure

Materials were dried to remove the moisture. Oily mill scale containing 24.6% oil was heated to 400°C to remove the oil. All the materials were crushed under 325 mesh. A waste mixture was prepared, representing the waste generated in ERDEMIR, containing 40% coarse mill scale, 20% BF sludge, 15% BF dust, 15% BOF sludge, 5% BOF dust and 5% oily mill scale. This mixture contained 57.2% total iron and 9.7% C.

Table 2. Chemical analysis (wt %) of the solid wastes generated in ERDEMIR with the production rates of wastes and binders (clinker and BF slag).

	BF Dust	BF Sludge	BOF Dust	BOF Sludge	Coarse Mill Scale	Oily Mill Scale	BF Slag	Clinker
Production (t/year)	61 000	81 000	20 000	60 500	160 000	22 000	—	—
% Fe <i>total</i>	30.00	42.06	43.24	56.00	74.49	48.20	0.52	2.48
% CaO	3.52	3.66	19.40	7.85	0.18	3.65	36.80	65.61
% SiO ₂	5.78	5.56	2.88	3.77	-	5.06	36.00	21.88
% Al ₂ O ₃	2.41	1.94	0.20	1.04	0.05	1.00	14.84	5.67
% C	25.56	29.30	-	-	-	-	-	-
% MgO	0.74	1.21	1.50	0.39	-	0.15	7.10	1.17
% Na ₂ O	0.082	0.05	1.58	0.095	0.012	0.35	0.30	0.25
% K ₂ O	0.15	0.17	0.74	0.12	-	0.025	0.81	0.83
% Zn	0.07	0.31	0.029	0.37	0.004	0.6	-	-
% Pb	0.01	0.03	0.003	0.04	0.007	0.01	-	-
% S	0.69	0.45	0.94	0.38	0.038	0.5	-	0.07
% Oil	1.19	2.39	-	-	-	24.60	-	-

Table 3. Chemical analysis of the reducing agents (wt %).

Reducing agent	C_{fix}	Volatile	Ash
Coke	81.22	3.31	15.47
Graphite	98.58	0.29	1.13

The waste mixture was pelletized after the addition of various amounts of the reducing agent, by using 6% BF slag and 4% clinker as the binder, and the pellets were aged under the optimum cold bonding agglomeration conditions. Details of the cold bonding agglomeration are given elsewhere (Çamcı & Aydın, 1997; Çamcı, 1998).

Cold-bonded pellets were reduced using an electrically heated laboratory scale rotary tube furnace of a total length of 1130 mm and an inside diameter of 80 mm. The reaction tube was rotated at

20-22 min^{-1} . Cold-bonded pellets were reduced under isothermal conditions in an argon atmosphere. Temperature measurement was carried out with a Ni/Ni-Cr thermocouple placed inside the reaction tube. The experimental setup is shown in Figure 1.

Experimental parameters were temperature, C_{fix} / Fe_{total} ratio, residence time and reducing agents. Experiments were conducted in the temperature range of 900-1100°C. The C_{fix} / Fe_{total} ratio can be described as the amount of carbon necessary to reduce completely the iron oxide that exists in the system. Reducing agents were used separately in the experiments and added to the mixture to give the same C_{fix} / Fe_{total} ratio. The C_{fix} / Fe_{total} ratio was selected to be between 0.17 (without reducing agent addition) and 0.45 which corresponds to 0.67-1.8 times the stoichiometric carbon. Table 4 lists the reduction test groups used in the experiments.

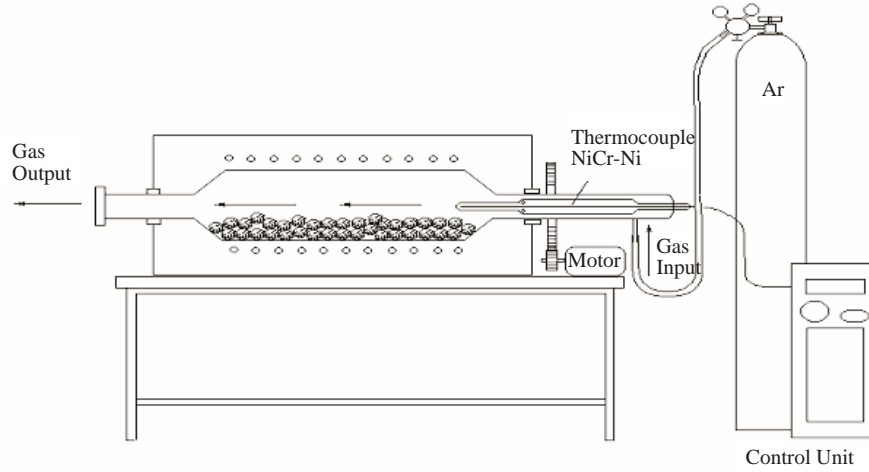


Figure 1. Experimental setup.

Table 4. Reduction test groups.

Amount of reducing agent addition		C_{fix} / Fe_{total}	Stoichiometric ratio (charged C / necessary C)
Coke %	Graphite %		
—	—	0.17	0.67
5	4.1	0.24	0.95
10	8.2	0.31	1.23
15	12.4	0.38	1.51
20	16.5	0.45	1.80

Experiments were started when the temperature reached the desired value. Pellets weighing 220 g were charged into the rotary furnace and argon was sparged in order to prevent re-oxidation during a reduction period of 120 minutes. Samples of the reduced pellets were taken every five minutes for the first 15 minutes of the experiment and every 15 minutes thereafter. Samples were placed in graphite crucibles in order to prevent oxidation and kept in a desiccator. Reduced samples were crushed, magnetically separated from char, and chemically analyzed for total iron.

There are several terms associated with the effectiveness of the reduction reaction. Since weight loss is caused both by the oxygen leaving iron oxides and by the gasification of the carbon containing reductants, it is difficult to calculate the “degree of reduction” of iron oxides with solid reductants from just the weight loss. Therefore, a simple formula has been recommended that can be used to obtain the degree of reduction. Equation (1) has been successfully used by other workers (Rahman, Haque and Haque, 1995; Mookherjee, Ray and Mukherjee, 1986; Haque, Ray and Mukherjee, 1992) to calculate the degree of reduction (R):

$$R = K \frac{\%Fe_{total}^r - \%Fe_{total}^i}{\%Fe_{total}^r \cdot \%Fe_{total}^i} \times 100 \quad (1)$$

where K = weight ratio of total iron to that of oxygen in initial waste mixture,

% Fe_{total}^i = percentage of total iron in initial waste mixture, and

% Fe_{total}^r = percentage of total iron in reduced mass.

Results and Discussion

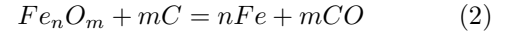
The process parameters of the reduction experiments were reaction temperature, C_{fix} / Fe_{total} ratio, type of reducing agents, and time. The degree of reduction vs. time data for the reduction reaction was obtained under controlled experimental conditions.

Effect of Temperature

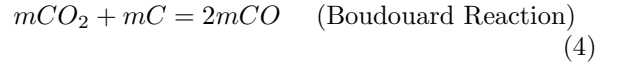
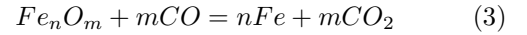
Reduction experiments of the composite pellets were carried out at 900, 950, 1000, 1050 and 1100°C with different coal consumption ratios. Figures 2 and 3 show the effect of temperature on the degree of reduction for C_{fix} / Fe_{total} ratios of 0.17 and 0.38. As

seen in the figures, the amount of reduction increases, for both C_{fix} / Fe_{total} ratios, as the temperature increases. As seen in Figure 3, a reduction period of approximately 60 minutes is satisfactory to reach a reduction degree of 0.7 at 1100°C, while it takes 110 minutes to reach the same degree of reduction at 900°C. A 22% increase in temperature reduces the reduction period about 45%. At the same temperature, on the other hand, for a degree of reduction of 0.5, a 22% increase in temperature causes a 67% decrease in time required for reduction. As seen, longer reduction periods are required at lower temperatures in order to reach the same reduction, and this period increases with the degree of reduction.

Reduction of iron oxides occurs either by carbon or by carbon monoxide, formed by the gasification of carbon. The reduction process carried out by the carbon is called “direct reduction”:



while the reduction process conducted with CO is called “indirect reduction”:



The overall reaction involves a cyclic mechanism in which CO₂ reduced as a result of the reduction of iron oxides gasifies carbon to generate CO, which in turn produces CO₂ through oxide reduction. The reduction and gasification reactions are thus necessarily coupled.

In order to reach a high degree of reduction, the temperature should be higher than 1000°C. Since the carbon gasification reaction (Boudouard reaction) is highly endothermic, a much larger amount of energy is required (Sharma, 1993). Thus, the rate of reduction is low at lower temperatures and the process does not reach completion.

Effect of Reducing Agents

In the sponge iron production experiments, coke and graphite were used as reducing agents. The first group of experiments was carried out without adding

any reducing agent. Carbon came from BF dust and sludge ($C_{fix} / Fe_{total} = 0.17$). In Figure 4, the degree of reduction is presented as a function of temperature for different C_{fix} / Fe_{total} ratios and at the 120th minute of isothermal reduction. According to Figure 4, without the addition of reduction agent at $C_{fix} / Fe_{total} = 0.17$ ratio, there was not a sufficient degree of reduction for the production of sponge iron. This was due to the low stoichiometric ratio (0.67). Also coke was more effective than graphite as a reducing agent in the production of sponge iron since coke's reactivity was higher than that of graphite at 1050-1100°C (Schlebusch, 1984).

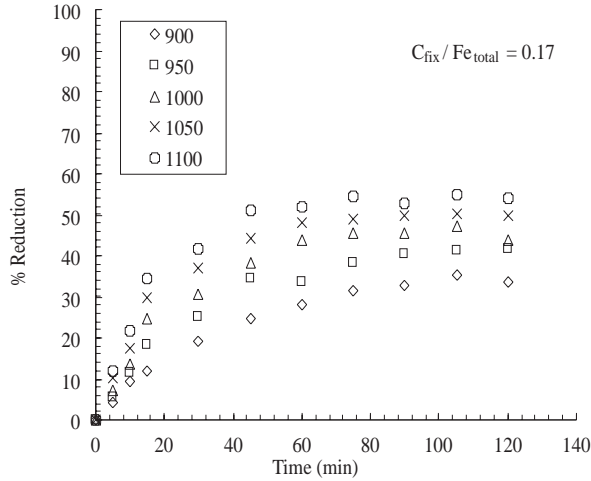


Figure 2. Reduction behavior of cold bonded pellets at different temperatures, having no reducing agent.

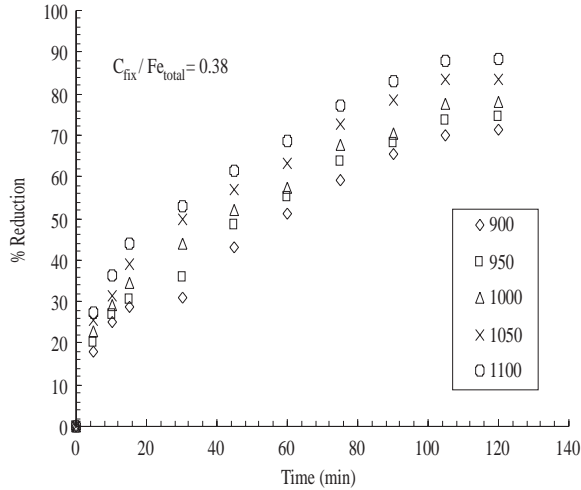


Figure 3. Reduction behavior of cold bonded pellets containing 15% coke powder as reducing agent, at different temperatures.

In the experiments where graphite powder was used, the highest reduction attained was 70% at 1100°C and at a C_{fix} / Fe_{total} ratio of 0.45. This reduction rate was achieved at a C_{fix} / Fe_{total} ratio of 0.24 when coke powder was used as a reducing agent, again at the same temperature.

Effect of C_{fix} / Fe_{total}

Reduction experiments were carried out at 0.17, 0.24, 0.31, 0.38 and 0.45 C_{fix} / Fe_{total} ratios. Figures 2 and 3 clearly indicate that increasing C_{fix} / Fe_{total} ratios cause an increase in the degree of reduction. Figure 5 displays the results of experiments carried out at different C_{fix} / Fe_{total} ratios. As seen from the figure, the required time for R=0.5 is 38 minutes at a C_{fix} / Fe_{total} ratio of 0.24, while it decreases to 20 minutes at a C_{fix} / Fe_{total} ratio of 0.45, indicating that the required time decreases about 90% when the carbon used is 87.5% more than stoichiometrically necessary. As can be seen, using more carbon than stoichiometrically necessary accelerates the reaction and decreases the time required for the reaction. For a degree of reduction of 0.8, on the other hand, the required time decreases about 35% with an 87.5% increase in C_{fix} / Fe_{total} ratio. When the C_{fix} / Fe_{total} ratio is 0.38, at R=0.8, in comparison with the C_{fix} / Fe_{total} ratio of 0.24, the decrease in time is about 31% by increasing the ratio 58%. This means that the same degree of reductions can be reached within a certain time period by adding fewer amounts of reducing agents. For the economics of the process and the environment, the reduction should be carried out at the optimum time and C_{fix} / Fe_{total} ratio. Thus, C_{fix} / Fe_{total} ratio is about 0.35 or the stoichiometric ratio should be about 1.4.

Kinetics of the Process

The results of the isothermal reduction of waste oxide are shown in Figure 3 for C_{fix} / Fe_{total} ratio of 0.38. In order to ascertain the appropriate kinetic equation, these results were checked against standard reduced time plots. In reduced time plots, the kinetic relationship are first expressed in the form

$$G(R) = k t \tag{5}$$

where G(R) is an appropriate function of R. If $t_{0.5}$ is the time required to obtain 0.5 fraction reacted, i.e. R=0.5, then

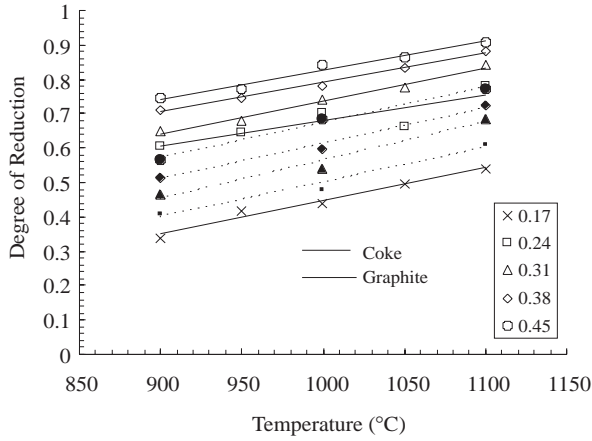


Figure 4. Effect of different reducing agents on the degree of reduction with increasing temperatures at different C_{fix} / Fe_{total} ratios at the 120th minute.

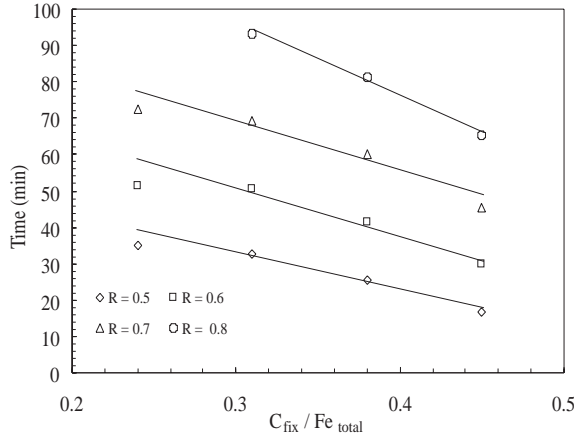


Figure 5. Effect of C_{fix} / Fe_{total} ratios on the degree of reduction with increasing time at 1100°C, using coke as reducing agent.

$$G(R)_{R=0.5} = kt_{0.5} \tag{6}$$

Dividing equation (5) by equation (6) one obtains the kinetic relationship in an altered form given as

$$G(R) = A(t/t_{0.5}) \tag{7}$$

where A is a constant dependent on the form of the function G(R). Equation (7) is independent of the kinetic rate constant and is dimensionless; thus, for a particular reaction mechanism, a single equation of this type represents all kinetic data irrespective of the nature of the system, temperature, or other factors that affect the reaction rate. Each mechanism,

therefore, has a unique reduced time plot (Mookherjee, Ray and Mukherjee, 1986).

To ascertain the appropriate kinetic law, first the functional values of G(R) for various values of different kinetic mechanisms are tabulated. These are then used to calculate $t/t_{0.5}$ values. Master plots for the various kinetic laws are obtained by plotting the R-values against the calculated values of $t/t_{0.5}$. Reduced time plots of experimental data are then superimposed on these in order to determine which theoretical plot fits the experimental data. Figure 6 shows the theoretical plots for three kinetic laws and experimental points from the isothermal plots presented in Figure 3. It is found that the experimental data would fit in the Ginstling–Brounshtein equation,

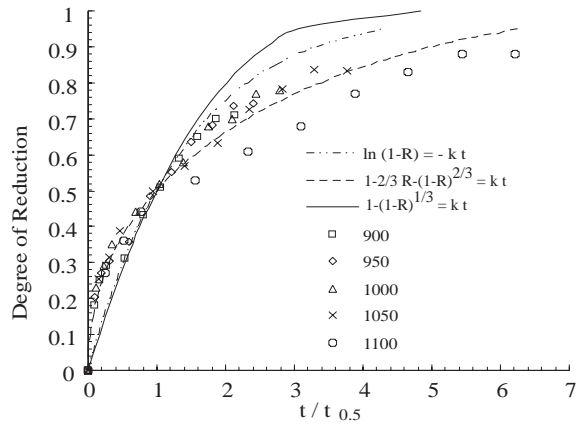


Figure 6. Experimental data compared with three different kinetic mechanisms.

$$G(R) = 1 - 2/3R - (1 - R)^{2/3} = kt. \tag{8}$$

Figure 7 shows the plot of experimental results according to the Ginstling–Brounshtein equation. This model shows that the reduction process was controlled by diffusion. The slopes of these lines yield the values of k at a given temperature. In order to obtain the activation energy value, the R-values were plotted according to the Arrhenius equation. Figure 8 shows the Arrhenius plot. The activation energy of the process was calculated as 48.5 kJ/mole from the slope of the line. Although the activation energy found may seem to be high for a diffusion controlled process, the iron oxide–carbon system is a complex one and, therefore, there is neither a general rate equation nor a clear cut method for the interpretation of kinetic data. In a number of studies

involving the iron oxide-carbon system, kinetic data obtained were found to fit the Ginstling-Brounshtein model (Rahman, Haque and Haque, 1995; Mookherjee, Ray and Mukherjee, 1986; Dey, Biswanath and Basumallick, 1993). The activation energy values they calculated, on the other hand, seem to be higher than those found in this study.

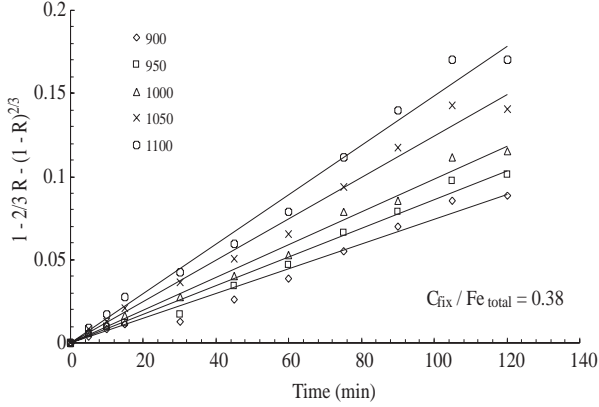


Figure 7. Experimental data correlated by the Ginstling-Brounshtein equation.

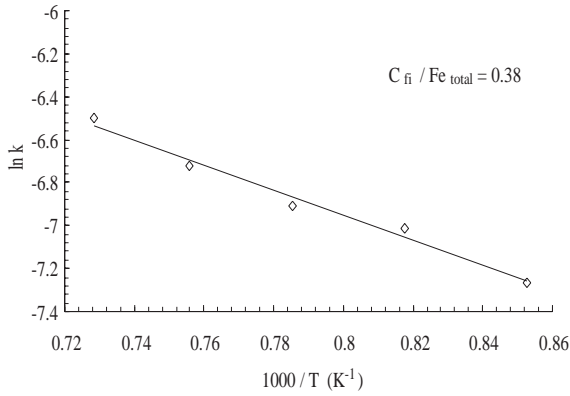


Figure 8. Arrhenius plot resulting from Figure 7.

Conclusion

One of the suggested methods for the beneficiation of iron oxide containing solid wastes, created by the integrated iron and steel works, is the production of cold-bonded pellets. Pellets produced by this method can be directly charged to the blast furnace. Another technique is the production of sponge iron from these wastes. The reduction behavior of cold-bonded pellets containing solid reductants was considered in this study in order to understand the possibility of using pellets directly in the blast furnace and/or in the production of sponge iron.

Higher reduction rates were attained by utilizing coke powder, another form of solid waste produced in integrated plants, as compared to the use of graphite powder.

With increasing temperature, the degree of reduction was increased and, in comparison, equal degrees of reduction were obtained in low reduction times. In order to reach a high degree of reduction, the temperature should be higher than 1000°C.

For the economics of the process and from the environmental point of view, the reduction should be carried out at the optimum time and C_{fix}/Fe_{total} ratio. In this study, this ratio is about 0.35 or the stoichiometric ratio should be about 1.4.

The kinetic study was carried out using coke as the reducing agent for the production of sponge iron. In order to obtain an initial idea of the kinetic law, reduced time plots were used. In these plots, three commonly suggested models for iron oxide reduction were used. The Ginstling-Brounshtein model seems to be the most appropriate to fit the data obtained from this study. This model shows that reduction was controlled by the diffusion of the reaction gas, and the activation energy of the process was calculated to be 48.5 kJ/mole from the slope of the line.

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