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Sponge Iron Production by Calcium Carbonate, Sodium Carbonate, and Barium Carbonate Catalysts Using Tunnel Kiln Method

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Abstract

Due to the high price of natural gas in the production of sponge iron, the overall cost of production is also high in gas methods. Coal methods are an appropriate alternative to gas methods, in which anthracite coal is used to produce sponge iron. The low price of anthracite coal, low water consumption and low utilization of natural gas are the reasons for the superiority of these methods. In this research, the production of sponge iron was investigated with calcium carbonate, sodium carbonate, and barium carbonate catalysts under different conditions using the tunnel kiln method. The results showed that sodium carbonate catalysts had the highest efficiency in the extraction of sponge iron from the coal. Also, decreasing the size of the catalyst particles increased the extraction of iron from the raw materials. With an increase in reduction time from 1 to 3 hours and an increase in the reaction temperature from 900 to 1100°C, the iron extraction was increased. The maximum iron extraction efficiency of 82.5% and 91.5% at reduction time = 8 hours was obtained for sodium carbonate catalysts in micrometers and nanometers scales, respectively.

Introduction

Increasing production with a view to lowering energy consumption is one of the main goals of steel mills in the world. Basic steel industries generally use iron ore for the production of steel. Recently, a direct reduction is an important step in the global steel industry. Iron ore direct reduction is an attractive alternative steelmaking process in the context of greenhouse gas mitigation [1]. There are various reasons for the growth and development of the direct reduction method. The problems of coke supply, lack of energy resources, currency problems, and sharp price fluctuations in scrap prices are the factors of growth and the importance of direct reduction. Direct reduction converts iron ore pellets into direct reduced iron, using a mixture of CO and H2 produced by reforming natural gas. Due to reduced investment costs, independence from coal and coke imports, and reduced construction time, direct reduction units are becoming more numerous, particularly in countries where cheap and abundant natural gas. A direct reduction method using tunnel kiln is one of the reduction methods that need a very low volume of water for the process in which sponge iron is produced. A tunnel kiln **(Figure1)** is a long stationary insulated furnace made of refractory bricks which has a rail track provision for trolley movement. Materials are filled inside the containers called saggers, which are placed on the trolleys that enter from the feed end and come out on the other end by traveling the entire length of the kiln with a prefixed speed. The kiln has three different zones called firing zone (reduction), preheat zone (warm-up), and cooling zone. The producer gas obtained from the coal gasifier is burnt in the firing zone through

the number of gas burners. The cooling of the material on the trolley is done by ambient air pumped by external fans and hot air from the cooling zone is utilized for drying of raw materials. The heat carried by the flue gas is recovered through the heat exchanger and utilized in the gas burners to preheat combustion air. The post-combustion of the in situ generated CO gas reduces producer gas consumption. Anthracite coal is also used to produce a reduction in gas. The oldest of these methods is Hoganas that was invented by E. Sieurin in Sweden in 1908 [1]. In this method, iron ore with coke or coal with calcium carbonate stones in a tunnel kiln at 1200 °C and the product with more than 70% iron is subsequently cooled down in the air and used as a metallurgical powder after separation its calcium carbonate and carbon [2]. In this method, regeneration is carried out inside the furnace and in the dishes made of incombustible shamut or silicon carbide or cast-iron dishes. The main purpose of the invention was to provide metallurgical powder for the steel industry. Later, this method was used for producing sponge iron also. The product of this method, in contrast to the usual direct reduction methods, such as Midrex and Hyl [3] which are in bullets with a diameter of 18 millimeters, is cylindrical and much higher weight and because of its high weight rather than the Midrex method, is rechargeable in induction furnaces. The Sponge iron produced by the Midrex and HyL method can be used for low induction hardness due to its low density. The reducing agent in all direct reduction systems is hydrogen and carbon monoxide. The carbon monoxide and hydrogen gas can be produced by the failure of natural gas in the vicinity of a catalyst or an incomplete combustion natural gas with oxygen. One of these methods is the use of coal for the production of reducing gas. The carbon monoxide gas is produced by burning coal and used for direct reduction. To increase production efficiency, catalysts are used in combination with coal [4], which reduces the recovery time and increases production. The main catalyst is calcium carbonate, which is used in all direct reduction units of the tunnel furnace [5].

In this research, the effects of sodium carbonate, calcium carbonate, and barium carbonate catalysts on the production of sponge iron from renewable materials including iron oxides were investigated. In the next step, parameters such as reduction time, the type of catalysts, particle size, and temperature of the reduction process were investigated in the iron extraction process.
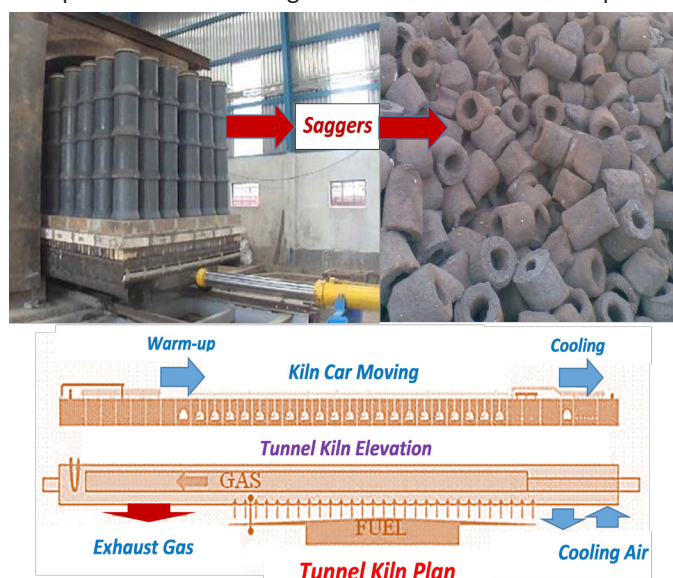

Figure 1: Schematic of the iron extraction process in a tunnel furnace.

Materials and Methods

Materials

Ferric chloride, ammonium chloride, potassium dichromate, sodium diphenylamine sulfonate, phosphoric acid, sulfuric acid, Sodium carbonate, barium carbonate, and calcium carbonate were obtained from Merck Co.. Anthracite coal was used from the Chamestan coal plant in Amol, Iran. Chadermollo iron ore concentrate and pellet grain concentrate of Ardakan Steel Co. was used for regeneration.

Experimental section

Initially, the raw powder was converted into spherical pellets with a diameter of 18 mm. Then it was coated with anthracite coal powder and certain wt. % catalyst in porcelain and placed in the furnace at temperatures between 900 ° - 1100 ° C in different periods of 1-3 hours **(Figure 2a)**. In the second section, scale-up experiments were also examined on an industrial scale. First, the raw powder was placed in a refractory chamotte vessel (Fig. 2b) and in the center and surrounding of it covered with a mixture of anthracite coal powder with various dimensions and various catalysts, and placed in the tunnel kiln at different temperatures.
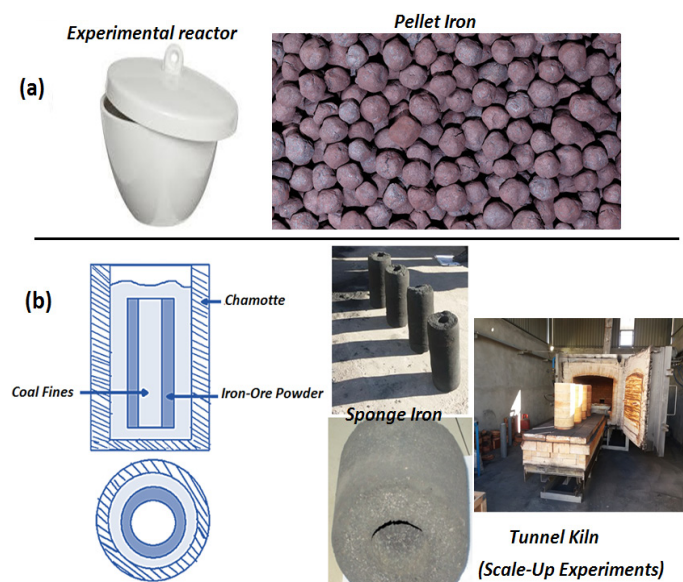

Figure 2: Experiments in **(a)** laboratory and **(b)** industrial scale.

For the conversion of different materials into nano-scale dimensions, the ball milling model HSG-100 Herzog was used. For calculating the amount of extracted iron this method was used: To convert the iron in the sample into detectable, ferric chloride and ammonium chloride was used, and to measure the number of iron molecules by titration way, potassium dichromate used. A solution of sodium diphenylamine sulfonate in phosphoric acid and sulfuric acid was used as the reagent. First, the sample of each experiment was crushed up to 400 mesh powder by a cylindrical ring mill. 0.1 gram of sample was poured into an Erlenmeyer containing 40 cc of 12% v/v ferric chloride solution with 20 cc of 10% v/v ammonium chloride solution. The mixture was placed into the mixer for 20 minutes and then poured into 10 cc aqueous solution of phosphoric acid, sodium diphenylamine sulfonate, and sulfuric acid. The sample solution was titrated with 0.1N potassium dichromate solution and the aubergine color indicated the end of the titration. The amount of iron was calculated by the following equation:

$$M = \frac{0.7185 \times V \times F}{W} \qquad (1)$$

Which, M is the percentage of iron extracted (Fe %), F is the concentration of potassium dichromate, V is the volume of dichromate consumed, and W is the sample weight in grams. To investigate the morphology and particle size of the materials Field Emission Scanning Electron Microscope (FeSEM) model HITACHI S-4160 was used.

Results and Discussion

The results of the tests performed in laboratory conditions are presented in Table 1. Experiments are carried out in the presence of different catalysts, temperatures and times, and the results are shown.

Table 1: Iron extracted at different temperatures and times for different catalysts.

Temperature (°C)	900			1000			1100		
Time (hr)	1	2	3	1	2	3	1	2	3
Catalyst Na2CO3	52	54	57	59	63	66	68	71	75
Catalyst BaCO3	5	10	11	14	16	18	40	42	49
Catalyst CaCO3	0	0	0	8	9	11	20	25	28
Without Catalyst	0	0	0	5	5	5	15	18	25

According to the results of Table 1, three sodium carbonate, barium carbonate, and calcium carbonate catalysts are used to reduce the samples, in which the best results are for sodium carbonate. Sodium carbonate, barium carbonate, and calcium carbonate showed the highest amount of iron extracted at all temperatures and at 1, 2 and 3 hours time, respectively.

Also, the lack of catalysts has reduced the iron extraction efficiency against any of the catalysts. The higher catalytic efficiency of sodium carbonate can be due to that the melting point of sodium carbonate is low and about 800 °C which is lower than the process temperature. Thus the time to reach the temperature of the sample to the furnace temperature reduces and the rate of reduction increases [6].

According to the results of **Figure 3**, the temperature has a positive effect on iron extraction. Iron extraction has increased with increasing reduction time. By increasing the opportunity to contact the reactants, mass transfer, reaction, and consequent iron extraction will increase.

Regarding the results of **Figure 4**, by decreasing the reduction process time the iron extraction has decreased too. Placing the sample at a longer time increases the material's contact time, facilitates the catalyst melting, and increases the reduction process efficiency.

The results illustrate that the sodium carbonate, barium carbonate, and calcium carbonate showed the highest efficiency of iron extraction, respectively. As the results of laboratory-scale tests, the catalytic efficiency of sodium carbonate is higher than the other two catalysts for the iron extraction process. To investigate the effect of catalyst particle size, sodium carbonate was used as the most efficient catalyst in nanometer and micrometer scales (Fig. 5) at different times, and the results were shown in Fig. 6. The results show that by decreasing the catalyst particle size from micrometer to nanometer, there is a significant increase in iron extraction. This could be due to an increase in the specific surface area in the nanoscale and, consequently, an increase in the number of active sites available for the iron re-
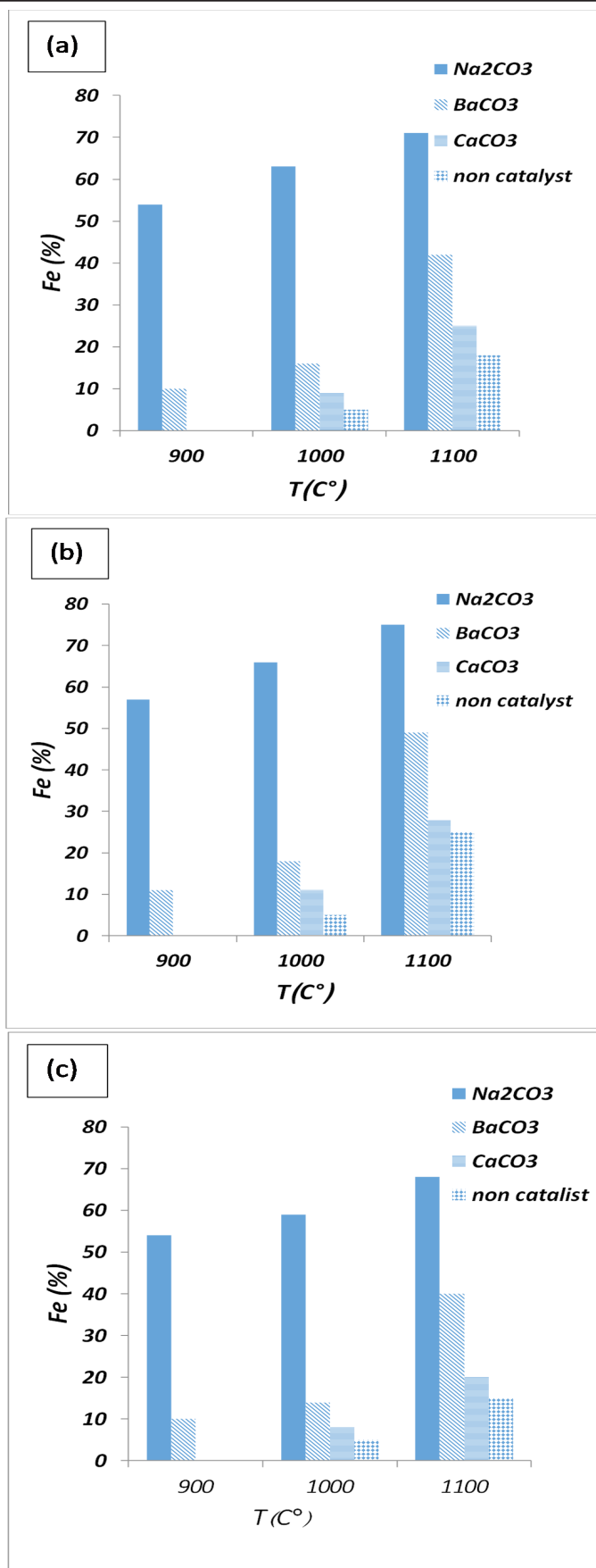
Figure 3: Effect of the reaction temperature on iron extraction at (a) 1, (b) 2, (c) 3 hr

duction process. Also, for both samples, the amount of iron extraction increased with increasing the reaction time **(Figure 5)**.
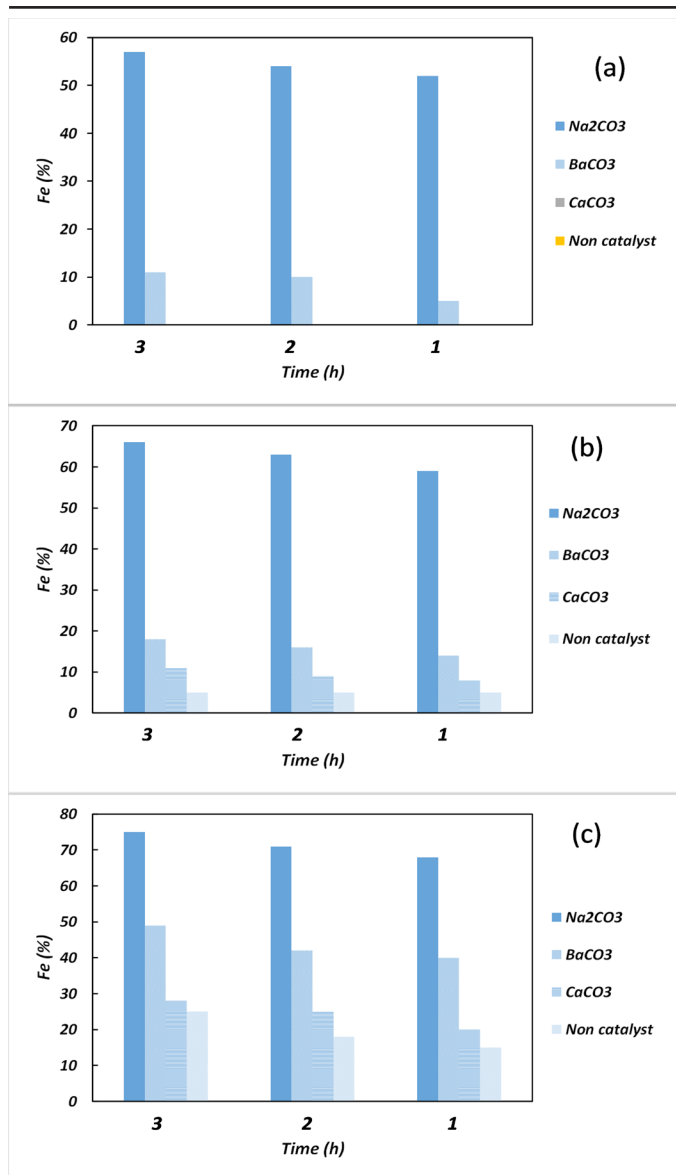
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Figure 4: Effect of reduction process time in iron extraction at (a) 900, (b) 1000, (c) 1100 °C.

Figure 5: Sodium carbonate catalyst at **(a)** and **(b)** micrometer scale and **(c)** and **(d)** nanometer scale.
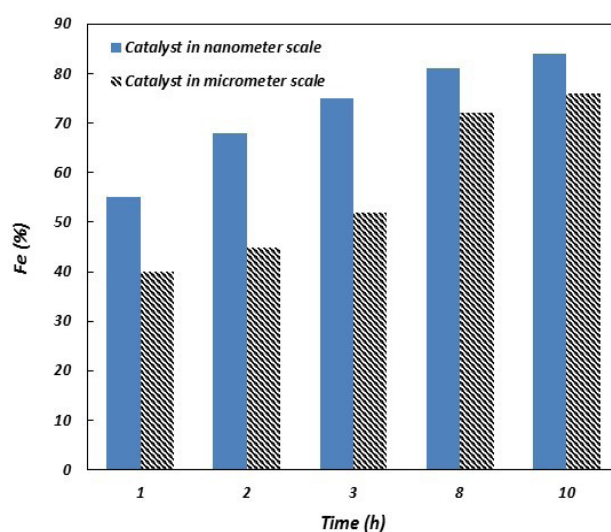
Figure 6: The percentage of iron extraction using sodium carbonate catalyst at different times.

According to the results of **Table 1**, the best result of iron extraction was for higher temperatures. Thus the industrial tests were performed at about 1100 °C. The results of tests on an industrial scale are presented in **Table 2**.

Table 2: Results of the industrial tests under different catalytic conditions.

Sample	CaCO3 Catalyst (wt%)	Na2CO3 Catalyst (wt%)	BaCO3 Catalyst (wt%)	Extracted Fe (%)
1	3	3	0	82.54
2	3	0	3	78.98
3	0	0	6	73.80
4	0	6	0	90.45
5	6	0	0	65.85

Conclusions

In this study, the production of sponge iron was investigated using calcium carbonate, sodium carbonate, and barium carbonate catalysts under different conditions using the tunnel kiln method. The results showed that sodium carbonate catalysts had the highest efficiency in the extraction of sponge iron compar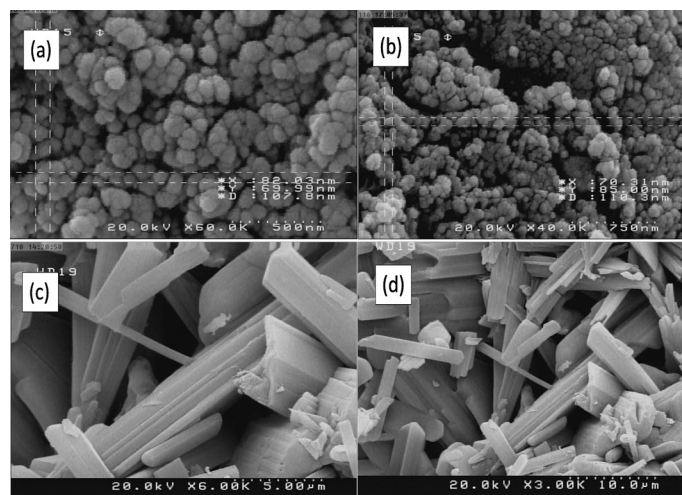ed to other catalysts used. Also, reducing the size of catalyst particles increased the extraction of iron from the raw materials, and the use of sodium carbonate nanoparticles in the reduction process, in addition to increasing iron extraction compared to other catalysts, reduced the reaction time of the resuscitation. Extraction of 82.5% and 91.5% of iron from the reduction material at 8 hours of recovery was obtained for sodium carbonate catalysts in micrometers and nanometers, respectively. Increasing the reduction time from 1 to 3 hours and increasing the reaction temperature from 900 to 1100C increased iron extraction.

Conflict of interest

We have no conflict of interest to declare.

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