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THE UTILIZATION OF THE PIDGEON PROCESS
FOR THE EXTRACTION OF MAGNESIUM FROM BLAST FURNACE SLAG

by

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A THESIS

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ABSTRACT

Blast furnace slag was used as feed for the production of magnesium by the Pidgeon process. With the operating variables at near optimum values, the Pidgeon process removed magnesium from the slag, but the yields were rather low. The low yields were caused by excessive amounts of silica in the slag. The removal of the silica from the slag appeared to be quite difficult. The use of blast furnace slag as a feed for the Pidgeon or other processes for the production of magnesium did not appear very promising unless a national emergency required huge production of magnesium with little regard to cost.

ACKNOWLEDGEMENTS

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CHAPTER I
INTRODUCTION

Magnesium is a metal that has been used extensively in military and commercial applications during the Twentieth Century, and it is estimated that the demands for magnesium will increase during the next decade (1)¹.

Magnesium is present in varying amounts in blast furnace slag, a by-product of integrated steel plants. (Slag generally contains between 8 and 15 per cent of magnesium oxide by weight; magnesium oxide contains 60 per cent of magnesium by weight.) This slag is available in huge quantities at relatively low costs.

Purpose of Investigation

The purpose of this investigation was to seek a method of economically removing magnesium from blast furnace slag.

¹Numbers in parentheses refer to references listed at the end of this paper.

CHAPTER II

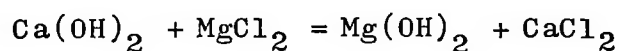
THEORETICAL CONSIDERATIONS

The first items to evaluate when considering the extraction of magnesium from blast furnace slags are the processes that can be used to extract this metal from materials.

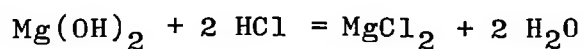
Electrolysis

During World War II the seawater electrolytic process was developed and accounted for the bulk of the United States' production of magnesium. This process is the most important method of magnesium production in the world today. It is performed in the following manner:

Seawater, which contains magnesium as a chloride, is agitated with slaked lime, and the following reaction occurs:



The magnesium hydroxide is precipitated and filtered away while the calcium chloride is pumped back into the ocean. The magnesium hydroxide is then treated with hydrochloric acid, and the following reaction occurs:



The magnesium chloride is then dried to form the feed for the electrolytic cells. The cells are steel shells which are heated to supplement the heat generated electrically in the cell; the temperature is maintained at approximately 725° C. during the process. Graphite electrodes enter the top of the cell and act as anodes while the steel body of the cell serves as the cathode. The typical electrolysis then occurs, and magnesium is liberated and floats to the top of the cell where it is periodically removed. The power requirement is 8 to 10 kilowatt-hours per pound of the metal (2).

While electrolysis has displayed commercial success, sufficient inherent objections to the method exist to justify a search for a better process. These objections are as follows (3):

1. Electrolysis is handicapped in the case of metals such as magnesium that are high in the electrochemical series since many natural impurities are less electropositive than the desired metal; therefore, they are deposited before the metal. For this reason, a very pure feed must be supplied to the electrolysis cell.
2. The electrolytic process requires huge

quantities of electricity. This requirement is particularly detrimental during war years when the need for electricity faces fantastic demands.

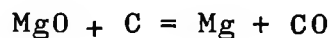
3. Chlorine must be handled at the electrolytic cell; this problem is solved most successfully if the magnesium plant is located adjacent to a complicated chemical arrangement.
4. Electrolysis requires anhydrous magnesium chloride which is extremely difficult to produce and handle.
5. The electrolytic plant is quite costly to build.
6. The purity of magnesium obtained from the electrolytic method is questionable.

The objections, combined with the fact that electrolysis requires magnesium chloride while the slag contains magnesium in the oxide form, make electrolysis an unacceptable process for the removal of magnesium from blast furnace slag.

The Hansgirg Process

The carbothermic or Hansgirg process has been used to produce magnesium during the past four decades. In this process, briquettes of calcined

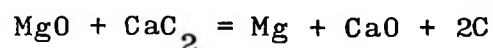
magnesite and carbon are placed in an electric arc furnace where the reaction



occurs with carbon removing the oxygen from the magnesium. The temperature required for the process is well above the boiling point of magnesium, and the magnesium and carbon monoxide vapor issue continuously from the furnace. Unfortunately, if the vapors are allowed to cool slowly, the reaction will reverse. To preserve the metal, the reaction vapors must be rapidly cooled as they leave the furnace; this cooling has been performed with hydrogen or natural gas. This cooling produces a very fine magnesium dust, carbon, and other substances. Subsequent vacuum distillation removes exceptionally pure magnesium from the mixture. The feed for this process must be quite high in magnesium oxide content - usually over 96 per cent - for satisfactory results (4). Since blast furnace slag contains much less magnesium oxide than this, the Hansgirg process would probably not remove magnesium from the slag in an efficient manner.

The Murex Process

The reaction of magnesium oxide with calcium carbide according to the equation

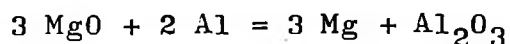


formed the basis of operation of Murex, Limited, in

England. The Murex process (as it has been called) required low vacuums and temperatures above 2200° F. The feed, calcined magnesite and calcium carbide, was heated in steel retorts in a gas-fired furnace; the magnesium distilled off and condensed in a cooling zone. A residue of solid carbon and calcium oxide was left. This process appeared very appealing; however, four tons of calcium carbide were required for every ton of magnesium produced, and the steel retorts had a very short life. The process proved uneconomical, and the plants at Murex have been closed (5).

The Aluminum Reduction Process

The reaction between solid magnesium oxide and metallic aluminum

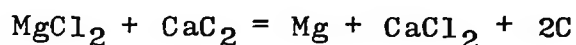


in vacuum at temperatures of approximately 2200° F. has been a basis of investigation and production in Russia and Norway. The high cost of the reducing agent, aluminum, has been a serious detriment to the process. While the use of ferro-aluminum and Al-silicon is feasible, both of these reducing agents are rather costly (4).

The Reduction of Magnesium Chloride by Calcium Carbide

The U. S. Bureau of Mines has studied the concept of producing magnesium by the thermal reduction of mag-

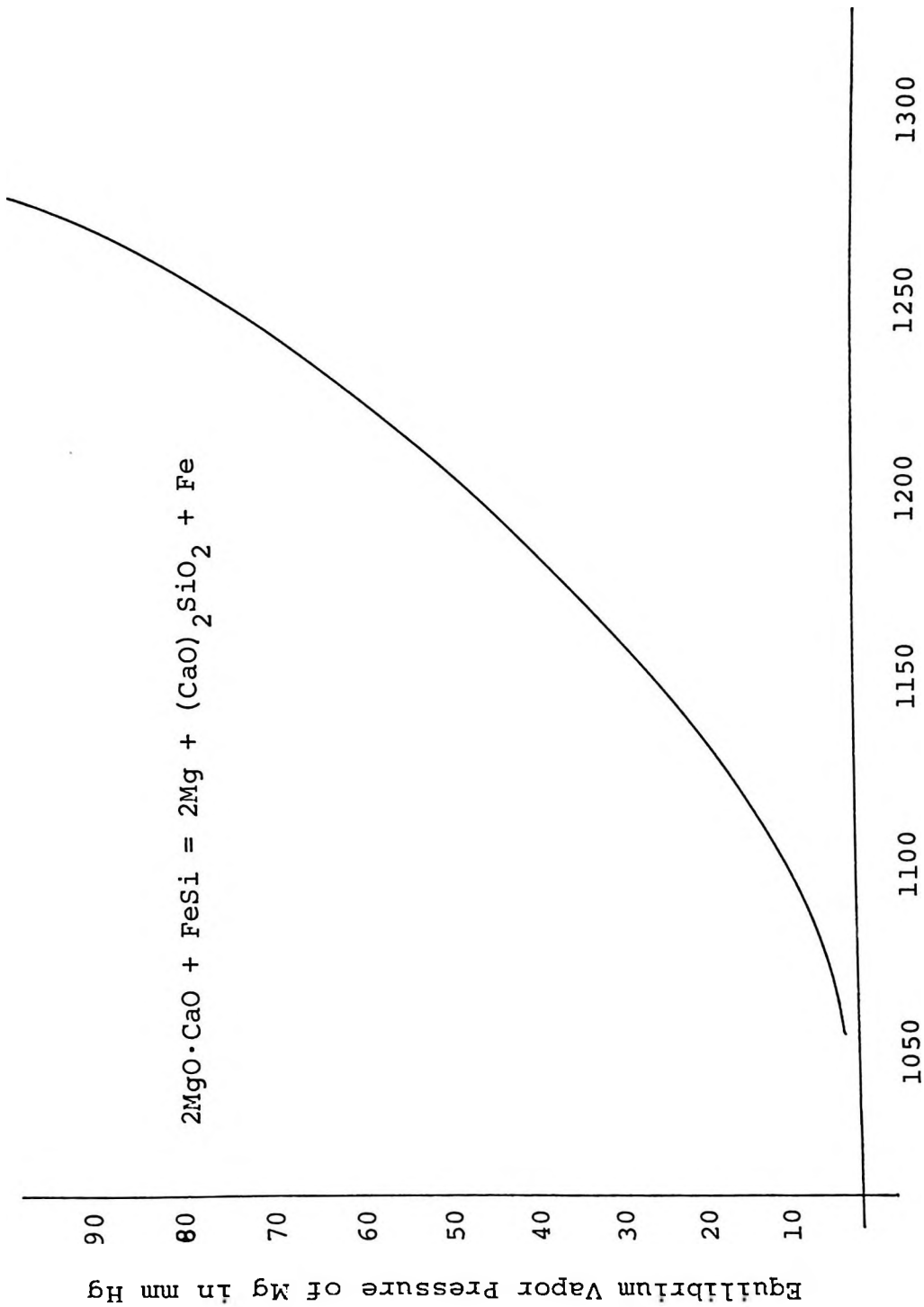
nesium chloride by calcium carbide according to the relationship (6)



While the previously discussed thermal methods required high temperatures and a vacuum system and were endothermic, this process occurred at ordinary pressures and lower temperatures and was exothermic. The reduction of the chloride with calcium carbide resulted in the magnesium being present as a framework of very small crystals which cemented the reaction residue. Separation proved to be an unsurmountable problem in this process (6).

The Pidgeon Process

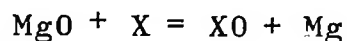
The search for a direct, thermal method of producing magnesium was conducted by a number of outstanding chemists and metallurgists. The most valuable experimental work was performed by a Canadian professor, Dr. L. M. Pidgeon, who carefully reviewed the known methods of freeing magnesium and then suggested the removal of magnesium from dolomite by reduction with silicon. This method of production, which became known as the Pidgeon process, utilizes the fact that magnesium is volatile at relatively low temperatures. (See Figure 1.) This physical property, which produces the great inflammability of the metal, allows the direct reduction of the oxide by



Temperature in Degrees C.

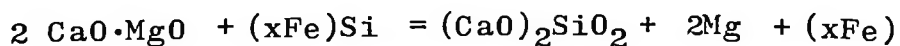
Figure 1 - Vapor Pressure Curve for Pidgeon Process (From Reference 7)

the basic reaction



which will yield magnesium vapor at high temperatures. The first reducing agent considered by Pidgeon was carbon because of its low cost and availability. However, carbon in this reaction produced a volatile oxide, CO, as well as the volatile magnesium. There was always danger of a back reaction unless the CO and magnesium were rapidly cooled; unfortunately, this rapid cooling yielded magnesium that was in the form of pyrophoric powder which was dangerous to handle and required redistillation before use. This, and other considerations, led Pidgeon to consider silicon as the reducing agent. Ferrosilicon was chosen as the form for the silicon because of its low cost (7). The decision to use dolomite as the source of magnesium oxide was reached because of the great availability of the rock, and because it contained lime that aided in the reaction.

Pidgeon concluded that the greatest possibilities for the thermal process were offered by the reaction between calcined dolomite and ferrosilicon which reacted according to the following equation (7):



In order for this equation or reaction to proceed, two basic requirements must be fulfilled. The

first is that the reducing agent must cause the production of an appreciable equilibrium vapor pressure of magnesium when the reducing agent and the magnesium oxide are heated to a sufficient temperature. The second requirement is that heat must be nearly constant. The first requirement is satisfied if the reaction is conducted in a vacuum or in a stream of hydrogen gas. Because of the safety involved, Pidgeon chose the vacuum system. Stated differently, the main function of the vacuum in the process is to lower the temperature at which the metal may be distilled or sublimed from the reaction mixture (7).

To obtain the feed for this process, Pidgeon found it necessary to have the dolomite and the ferrosilicon finely ground and then pressed into a briquette form. Grinding to fairly small size was required to permit the reaction to proceed to completion. Obviously, in the powdered form, any large-scale reaction would have been impossible since heat could not have penetrated into the mass nor could the magnesium vapor have escaped (7).

Pidgeon was very successful in freeing magnesium from dolomite by a thermal process. The process was valuable enough to be a great asset in America's drive for greater magnesium production during World War II and the Korean War. The Pidgeon process has remained a method of magnesium production during

times of peace.

Evaluation of the Processes

The only process that appeared valuable for the extraction of magnesium from blast furnace slag was the Pidgeon process. Electrolysis and reduction by calcium carbide require magnesium chloride for a feed, and magnesium is in the oxide form in blast furnace slag. The Hansgirg process requires a much higher concentration of magnesium oxide than is contained in blast furnace slag. The Murex process and the reduction by aluminum process have inherent problems that make them unacceptable.

Hence, the Pidgeon process was chosen as the process of experimental study.

CHAPTER III
MATERIALS AND EQUIPMENT

Materials

The slag used as feed for the Pidgeon process was produced by the Fairfield, Alabama, blast furnaces of the U. S. Steel Corporation. The laboratory at U. S. Steel (in Fairfield, Alabama) gave the following chemical analysis to the test slag samples:

TABLE I

Slag Chemical Analysis	
SiO ₂	34.04 per cent
Al ₂ O ₃	13.70
MgO	13.58
CaO	35.58
FeO	0.81
MnO	0.30
S	0.94
Others	1.05

When the slag was obtained from the U. S. Steel Corporation, it displayed the following sieve analysis:

TABLE 2
Slag Sieve Analysis

<u>Mesh</u>	<u>Per Cent Passing</u>
8	All
16	98.8
30	96.3
50	61.7
100	30.4
200	14.2

Equipment

It was necessary to locate or build a Pidgeon process plant; in this case a plant was in close proximity. The authorities at this plant, which is owned by the Alamet Division of the Calumet and Hecla Corporation and is located in Selma, Alabama, were most agreeable in allowing the use of the facilities for this research.

A typical Pidgeon process retort and furnace are shown in Figure 2. The Alamet plant uses steam ejectors for maintaining the vacuum during the process, and natural gas is the fuel used for maintaining the temperatures. The temperatures are measured by a simple thermocouple system.

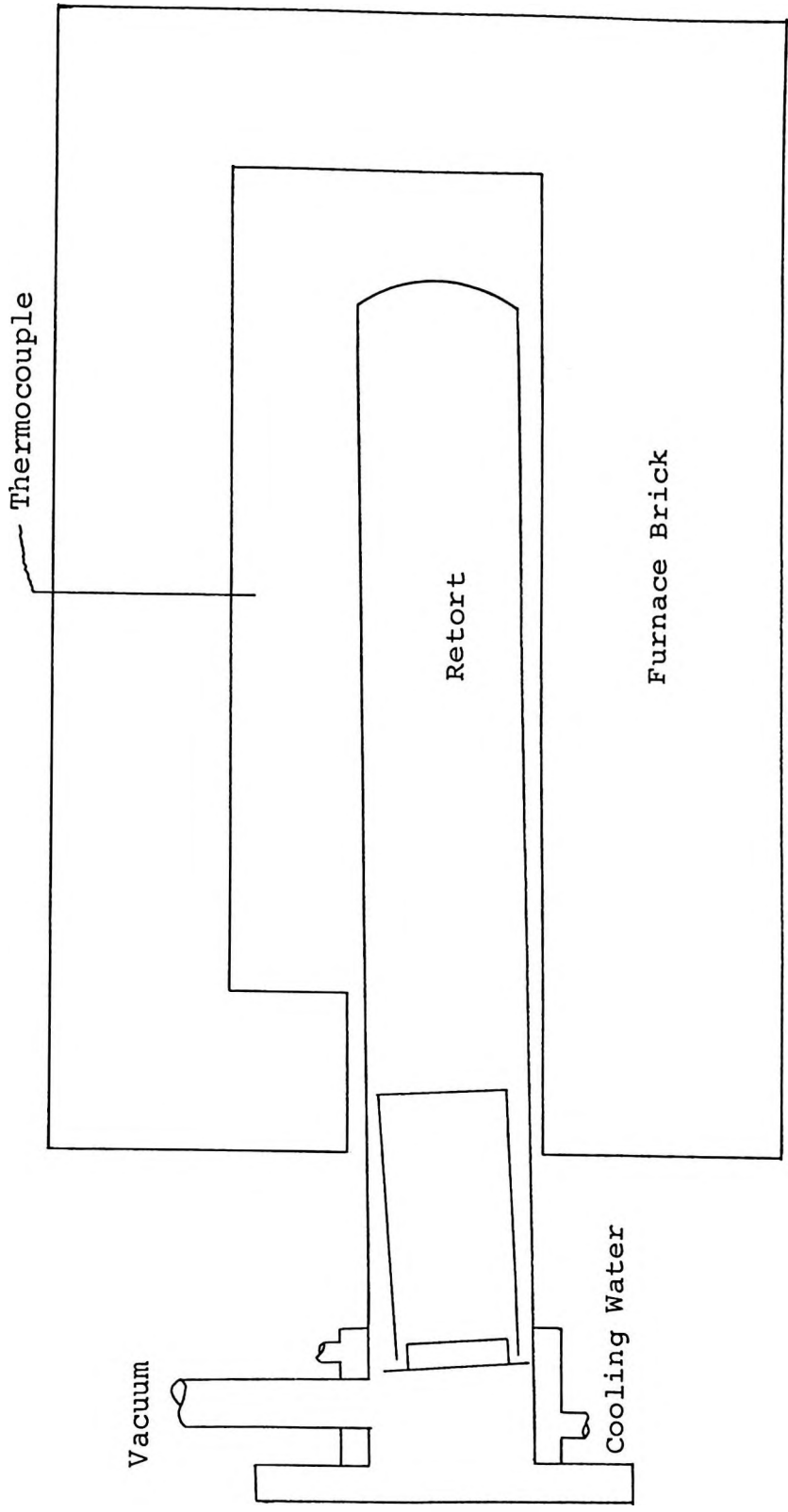


Figure 2 - Pidgeon Process Retort

CHAPTER IV

EXPERIMENTAL PROCEDURES

The slag was obtained and transported to the Alamet plant. It was necessary to select certain operational variables for the experiments in the Pidgeon process.

Particle Size

The particle size for the slag was a very important item. Since all the reactants of the Pidgeon process are solid, it would seem reasonable to expect better results with feeds that are finely ground. However, work by Pidgeon pointed to the fact that it is not necessary to grind the reactants finer than 100 mesh (7). This is also the opinion of the operators at the Alamet plant. Only slag that passed through the 100 mesh sieve was used in the experiments; a simple ball mill was used to grind the slag. (Chemical analysis performed on the slag that passed through the 100 mesh sieve were almost identical to the analysis of the slag in the as received condition.)

The reducing agent of the Pidgeon process, ferrosilicon, had to possess proper particle size for

successful operations. Using the same logic as in the case of the slag, it would seem that better results would be obtained if the ferrosilicon were finely ground. Again, former experimental work and the experience of the Alamet plant personnel indicated that this relationship was true only through the 100 mesh size. It seems to be vital that the magnesium-bearing material and the reducing agent be of nearly equal size. The ferrosilicon used was of the same size criteria as the slag.

A catalyst is used in the Pidgeon process, and it was ground to the same size as the slag and the ferrosilicon.

Reducing Agent

The grades of ferrosilicon that are available commercially vary from low values up to 95 per cent (silicon). Experimental data point to the fact that only grades above 75 per cent are acceptable because the lower grades yield slow reaction rates. The data further indicate that the 95 per cent grade is superior, but the extremely high costs of grades above 85 per cent rule them unavailable (7),(8),(9). The grade to be used was confined to the area between 75 and 85 per cent. In order to aid the experimental production, it was desirable to use the highest

grade of ferrosilicon available. A ferrosilicon of 82 per cent grade was selected. (This was the highest grade in supply at the Alamet plant.)

Catalyst

With the magnesium-bearing material and the reducing agent in proper condition, the need for a catalyst in the operation was considered. The work of experimenters in this area led to the opinion that a small amount of fluorspar aided the reaction of the Pidgeon process (7),(8),(9). (Fluorspar is essentially calcium fluoride, CaF_2 .) The advantages of fluorspar as a catalyst are illustrated in Figure 3 (7). Because of the evaluation of this graph and the operations records at the Alamet plant, it was decided to use 2-1/2 per cent fluorspar in the feed. No other catalysts were considered since all previous work on the Pidgeon process has failed to produce a better catalyst.

Proportioning the Feed

With the slag, ferrosilicon, and fluorspar ready for briquetting, the proportions to be used were determined. It is seen that 0.350 pound of silicon is required for each pound of magnesium oxide to be reduced. From the basic equation of the

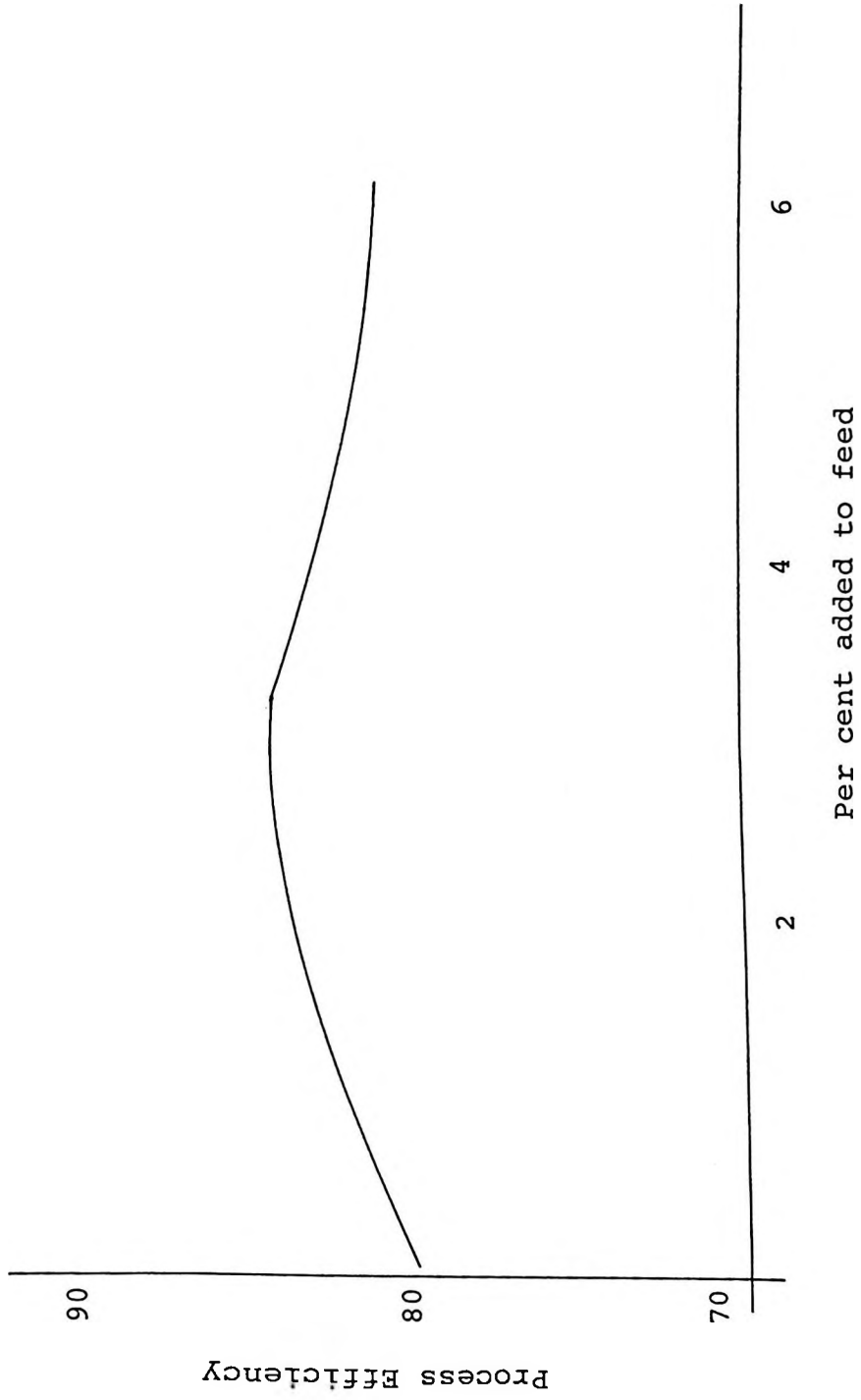
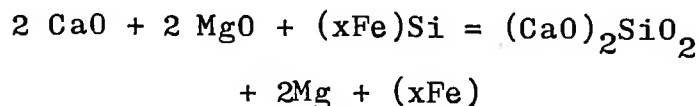


Figure 3 - The Effect of Fluorspar on Pidgeon Process Efficiency
(From Reference 7)

Pidgeon process,



this value is obtained.

$$\frac{\text{Si}}{2 \text{ MgO}} \times \frac{28}{2(24+16)} = \frac{0.350 \text{ \#Si}}{\text{\# MgO}}$$

The slag contains only 13.58 per cent magnesium oxide by weight (using the analysis from the U. S. Steel laboratory). There will be a need for 0.04753 pound of silicon for each pound of slag.

$$\frac{0.350 \text{ \#Si}}{\text{\#MgO}} \times \frac{0.1358 \text{ \#MgO}}{\text{\# Slag}} = \frac{0.04753 \text{ \#Si}}{\text{\#Slag}}$$

Since the ferrosilicon contained only 82 per cent silicon, it is obvious that more ferrosilicon is required than shown in the theoretical requirements of silicon. Additionally, excess silicon was used in the feed to insure sufficient reducing agents. With this as a guide, an excess of 35 per cent silicon was used; this made the silicon requirement 0.064165 pound per pound of slag.

$$\frac{0.064165 \text{ \#Si}}{\text{\#Slag}} \times \frac{(1.00 + 0.35)}{\text{\#Slag}} = \frac{0.064165 \text{ \#Si}}{\text{\#Slag}}$$

As indicated, the source of silicon, ferrosilicon, contained only 82 per cent silicon; the amount of ferrosilicon required was 0.0782 pound per pound of slag.

$$\frac{0.064165 \text{ \#Si}}{\text{\#Slag}} \times \frac{1 \text{ \#FeSi}}{0.82 \text{ \#Si}} = \frac{0.0782 \text{ \#FeSi}}{\text{\#Slag}}$$

The size of the retort was the determining factor in the size of charge to be tested. The retort used was capable of carrying a 20-pound charge quite handily, and this was the size selected. The constituents of the charge were determined.

Slag 18.1 pounds

Ferrosilicon 1.4

Fluorspar 0.5

$$\text{Fluorspar } \frac{20\# \text{ Feed}}{\text{Charge}} \times \frac{0.025\# \text{ Fluorspar}}{1\# \text{ Feed}} = \frac{0.5\# \text{ Fluorspar}}{\text{Charge}}$$

$$\text{Slag } 20.0 - 0.5 = 19.5\# \text{ remaining charge} \\ (\text{slag} + \text{ferrosilicon})$$

$$\frac{19.5\# (\text{slag} + \text{FeSi})}{\text{charge}} \times \frac{\text{charge}}{(1.0782)(\text{slag} + \text{FeSi})} \\ = \frac{18.1\# \text{ Slag}}{\text{charge}}$$

$$\text{Ferrosilicon } 20.0 - (18.1 + 0.5) = \frac{1.4\# \text{ Ferrosilicon}}{\text{charge}}$$

Blending the Feed

With these data, the blending or mixing of the ingredients began. Obviously, proper mixing (prior to briquetting) of the slag, ferrosilicon, and fluorspar were strict requirements. To insure adequate mixing, a "Y" shaped rotating blender was used; this device operated at 41 R.P.M. for 20 minutes. After this blending, the ingredients were considered to be adequately mixed.

Briquetting the Feed

The next step in the sequence was briquetting the mixture. (The need for briquetting was discussed earlier.) A decision had to be made as to the use of dry or wet briquetting. Wet briquetting offered the advantages of stronger briquettes, but it yielded a product that must be placed through a dehydration step before use. Additionally, wet briquetting did not produce as dense a briquette as did the dry method. These factors have influenced all commercial practices to the degree that only dry briquetting has been used. For the same reasons, dry briquetting was used in these experiments. The dry briquetting was performed in a high pressure roll press designed for this type of operation; the pressure used was 2100 pounds per square inch. This press yielded a briquette with a specific gravity of approximately 2.0 grams per cubic centimeter, which was quite sufficient when compared to the normal Pidgeon process feed which has a value of 1.90 grams per cubic centimeter. This briquette should have yielded good results since most of the published work on the Pidgeon process has indicated better efficiencies with higher densities (7), (8), (9). (Naturally, more magnesium was available per

unit volume because pores and spaces were removed by higher pressures and densities.) That the pressure of 2100 pounds per square inch was sufficient is shown by a graph of briquetting pressure versus efficiencies in the Pidgeon process (8). (See Figure 4.)

Little will be gained by increasing the briquetting pressure above the value of 2100 pounds per square inch.

Temperature of the Reaction

With the briquettes ready for the retorts, the problem of the temperature to be used was approached. It was known that this reaction can be carried out quite rapidly at 2000° F. under favorable conditions. It was proven by several investigators that greater efficiencies were possible at higher temperatures (7), (8), (9). The advantages of higher temperatures and the need for fuel utilization and savings combined to yield the use of 2150° F. for the Alamet process. This temperature served adequately, but the desire to make conditions as favorable as possible for the experiments led to the use of 2200° F. for the temperature. Certainly, this temperature was adequate to give the blast furnace slag feed very favorable conditions; this fact is obvious from

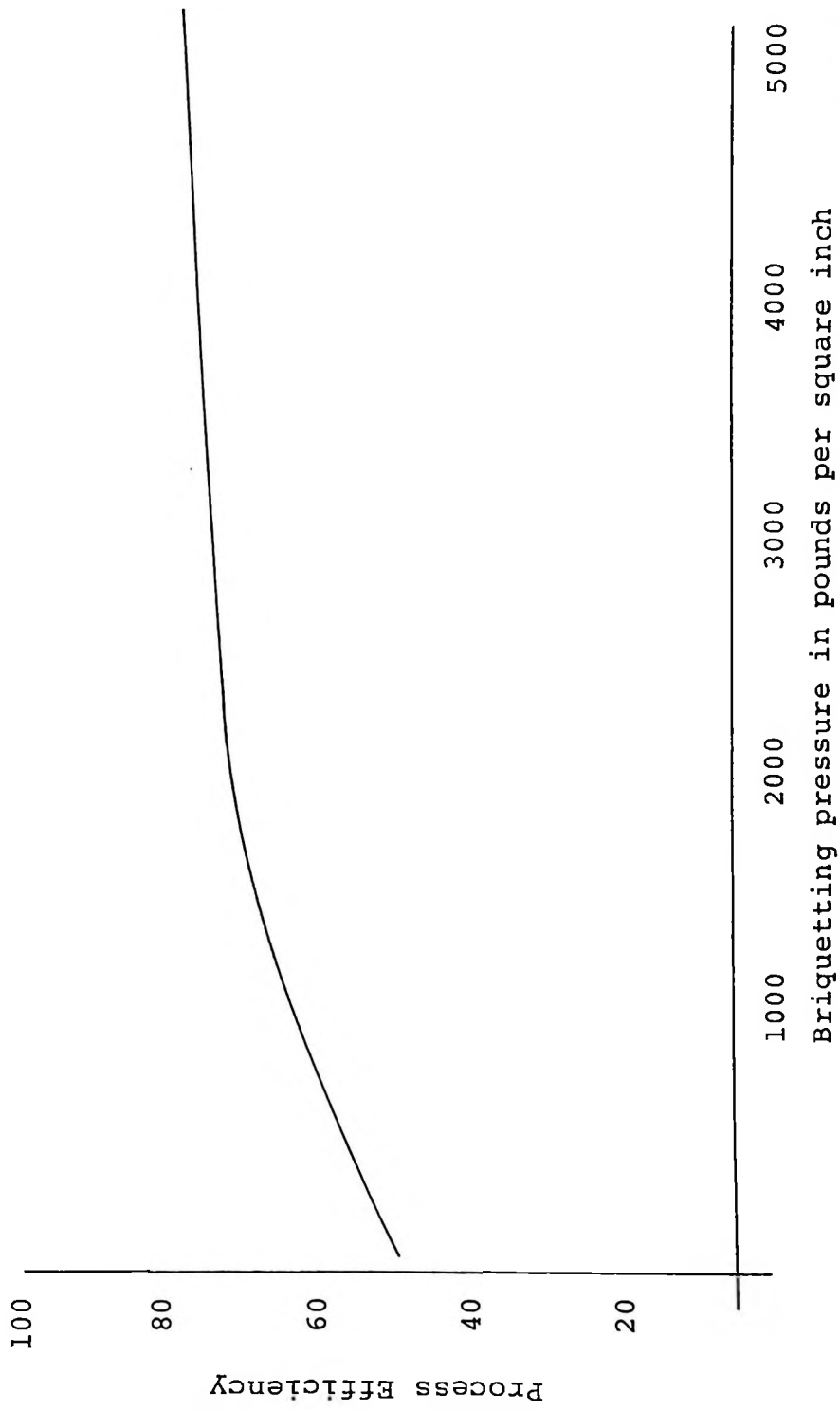


Figure 4 - The Effect of Briquetting Pressure on Pidgeon Process Efficiency
 (From Reference 8)

Figure 5, a plot of process efficiencies versus process temperatures (9).

Pressure for the Reaction

The next variable to consider was the proper vacuum to be employed in the process. Obviously, lower pressures, up to a point, yield better results in terms of process efficiencies. This relationship has been shown by research published in a recent paper (8), as indicated by the following plot of efficiencies versus pressure, Figure 6. This relationship does not hold true for pressures below 0.1 mm of Hg. Between 0.1 mm of Hg and 0.002 mm of Hg, little or no differences in the weight of the product yield can be observed (7). For this reason, the pressure used for the tests was 0.1 mm of Hg.

Time of the Reaction

The efficiency of the Pidgeon process is very dependent upon the time that the reaction is allowed to continue at the determined pressure and temperature. This fact has been known and published for several years, as is acknowledged by the plot of efficiency versus time as is shown in Figure 7. It is seen that near maximum values are obtained in 8 hours; additional time has shown only slight improvements in yield. Naturally, in commercial practice this time cycle will be kept as low as

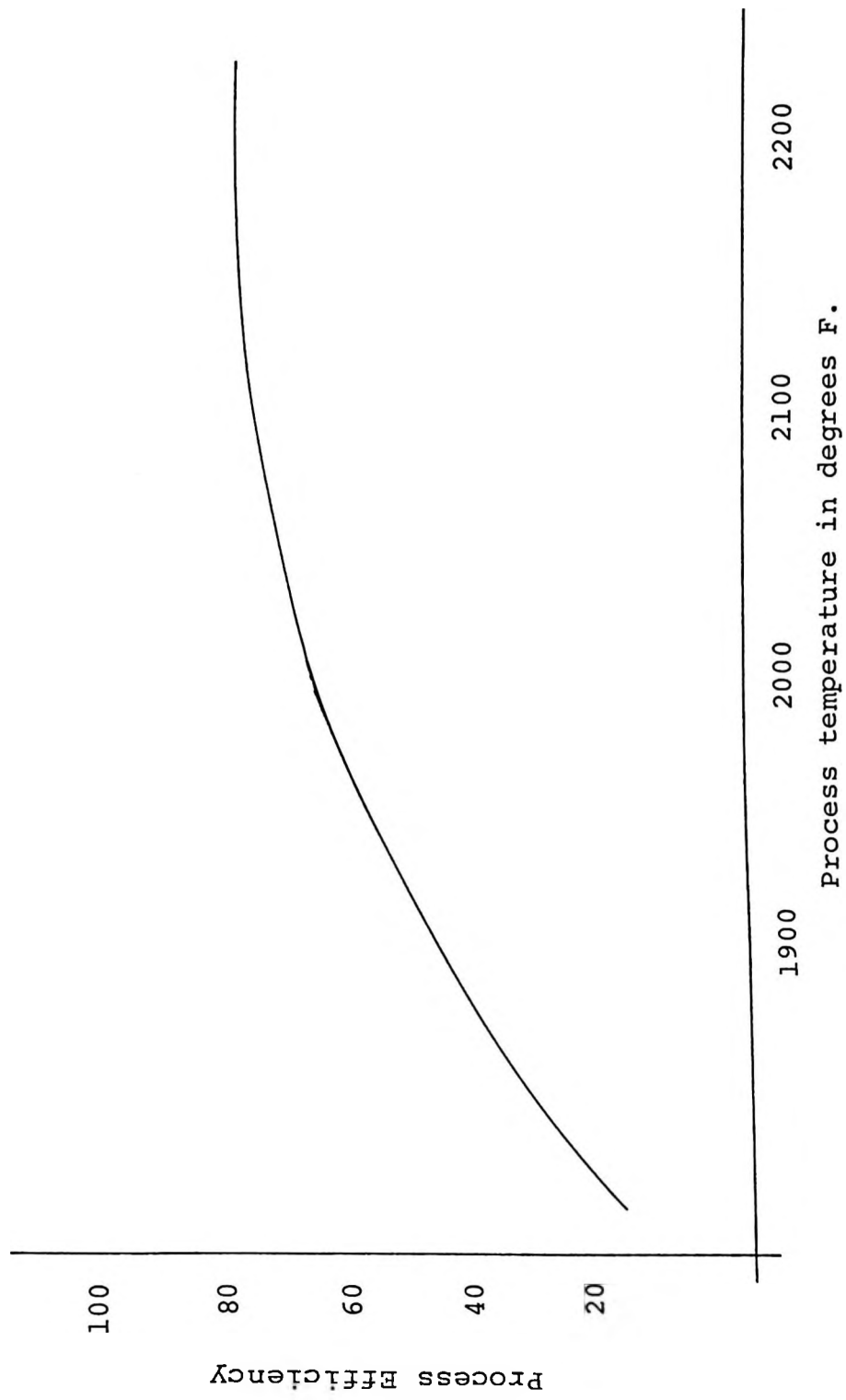


Figure 5 - The Effect of Temperature on Pidgeon Process Efficiency
(From Reference 9)

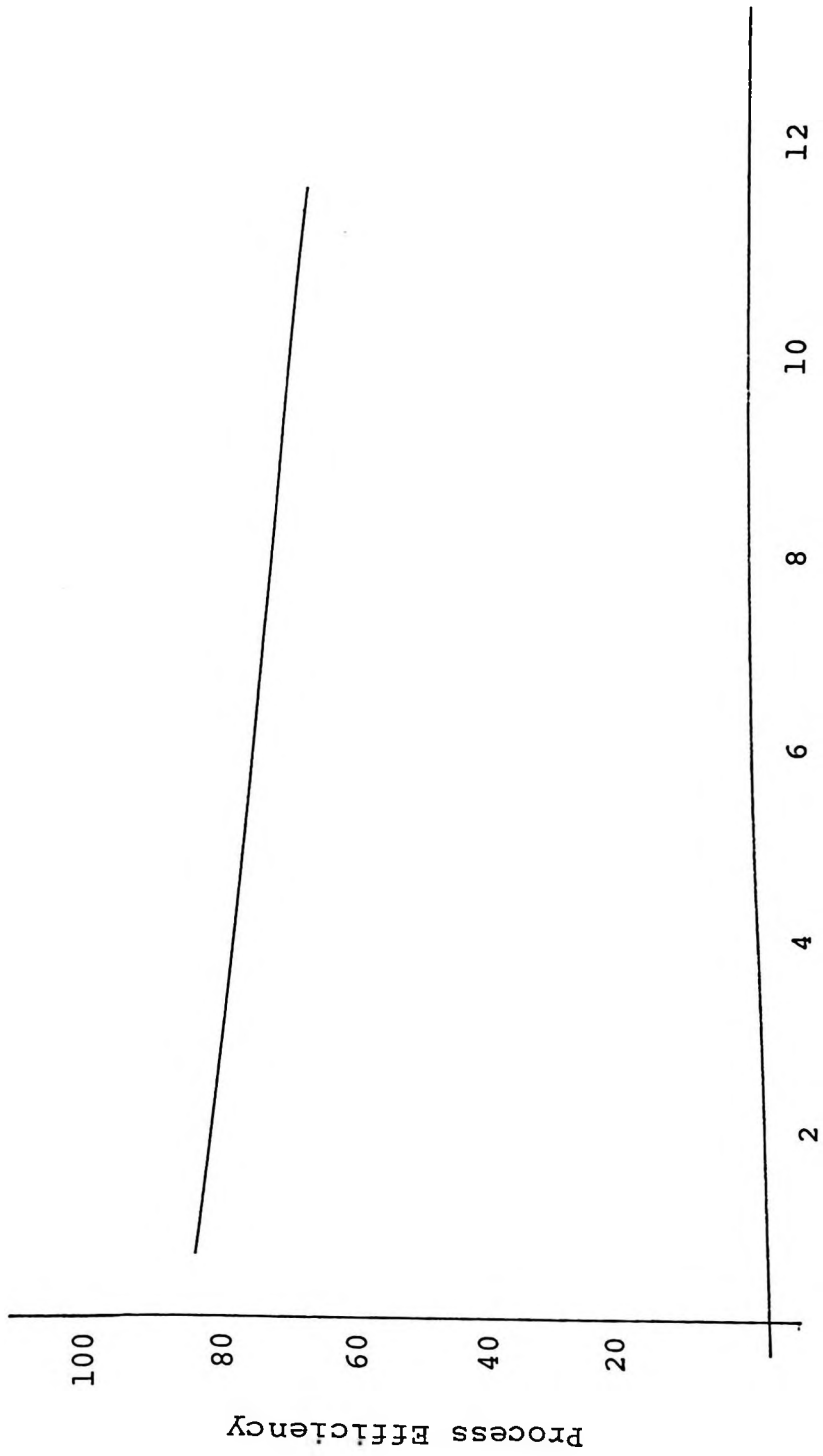


Figure 6 - The Effect of Pressure on Pidgeon Process Efficiency
 (From Reference 7)

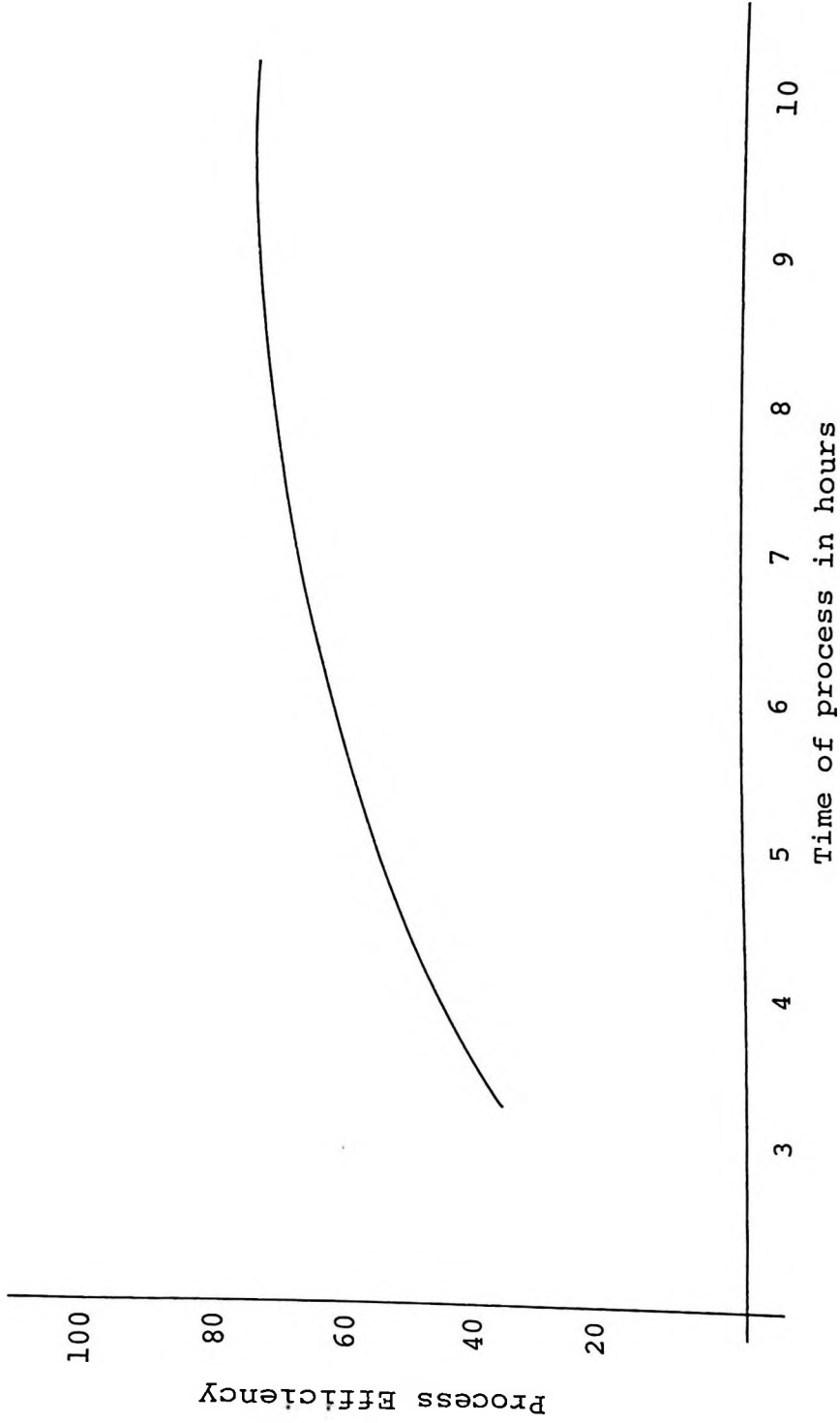


Figure 7 - The Effect of Time on Pidgeon Process Efficiency
(From Reference 9)

possible. A time of 8-1/2 hours was used to give test runs the greatest chances for success.

The Experimental Trials

With the feed properly prepared and the operating parameters carefully chosen, the experiment was begun in the retorts. As noted above, 18.1 pounds of slag were in the feeds; this represented 2.46 pounds of magnesium oxide. It should be noted that the slag contained 13.58 per cent magnesium oxide.

$$18.1 \text{ \# Slag} \times \frac{0.1358 \text{ \# MgO}}{\text{\#Slag}} = 2.46 \text{ \# MgO}$$

And this amount of MgO contained 1.48 pounds of magnesium.

$$2.46 \text{ \# MgO} \times \frac{\text{Mg (24)}}{\text{MgO (24 16)}} = 1.48 \text{ \# Mg}$$

At 100 per cent process efficiency, 1.48 pounds of magnesium would have been yielded from the retort.

CHAPTER V
RESULTS AND DISCUSSION

Process Efficiency

When the 8-1/2 hour time cycle was completed, the yield was a disappointing average value of 0.022 pounds of magnesium (9.9 grams). The amount of magnesium liberated from the slag ranged from values of 0.015 pounds (4.8 grams) to 0.029 pounds (15.9 grams), or from approximately 1 per cent to 2 per cent efficiency with the average efficiency being approximately 1-1/2 per cent. The data from four test runs are listed in the following table:

TABLE 3

	Data From Experimental Trials			
	<u>Test 1</u>	<u>Test 2</u>	<u>Test 3</u>	<u>Test 4</u>
Temperature	2200 F.	2200 F.	2200 F.	2200 F.
Pressure	0.10 mm Hg	0.08 mm Hg	0.15 mm Hg	0.10 mm Hg
Time	8-1/2 hrs.	8-1/2 hrs.	8-1/2 hrs.	8-1/2 hrs.
Yield	4.8 gm.	10.1 gm.	9.7 gm.	15.9 gm.

Effect of Silica

The low yields were undoubtedly the result of slag composition since all the variables of the process (temperature, time, pressure, catalyst additions,

and briquette quality) were maintained at near optimum values. The high ratio of calcium oxide to magnesium oxide was not the factor that produced the low yields because low grade dolomite and limestone with higher ratios of calcium oxide to magnesium oxide have been used successfully in the Pidgeon process (10). The amount of alumina present in the slag has not been detrimental to the process where large quantities of alumina (Al_2O_3) have been present (11). The large amount of silica (SiO_2) found in the slag must have been the item that caused the low yields. The only reference to silica (SiO_2) found in the literature was made by Dr. Pidgeon in 1944 (7). His work indicated that silica or insolubles in the feed acted merely as a diluent when present in small quantities but notably depressed the yields when present in large quantities. As is shown in Figure 8, Pidgeon did not complete the work on the effect of silica, since he only evaluated the effect of silica to values of 14 per cent (7). (This was quite high enough when considering dolomite as the feed, but inadequate when considering blast furnace slag.) It appears that the plot (See Figure 8) is nearly linear in Pidgeon's evaluations. Yet, a linear relationship to the value of 34.04 per cent silica (the amount present in blast furnace slag) still shows an efficiency of 20.7

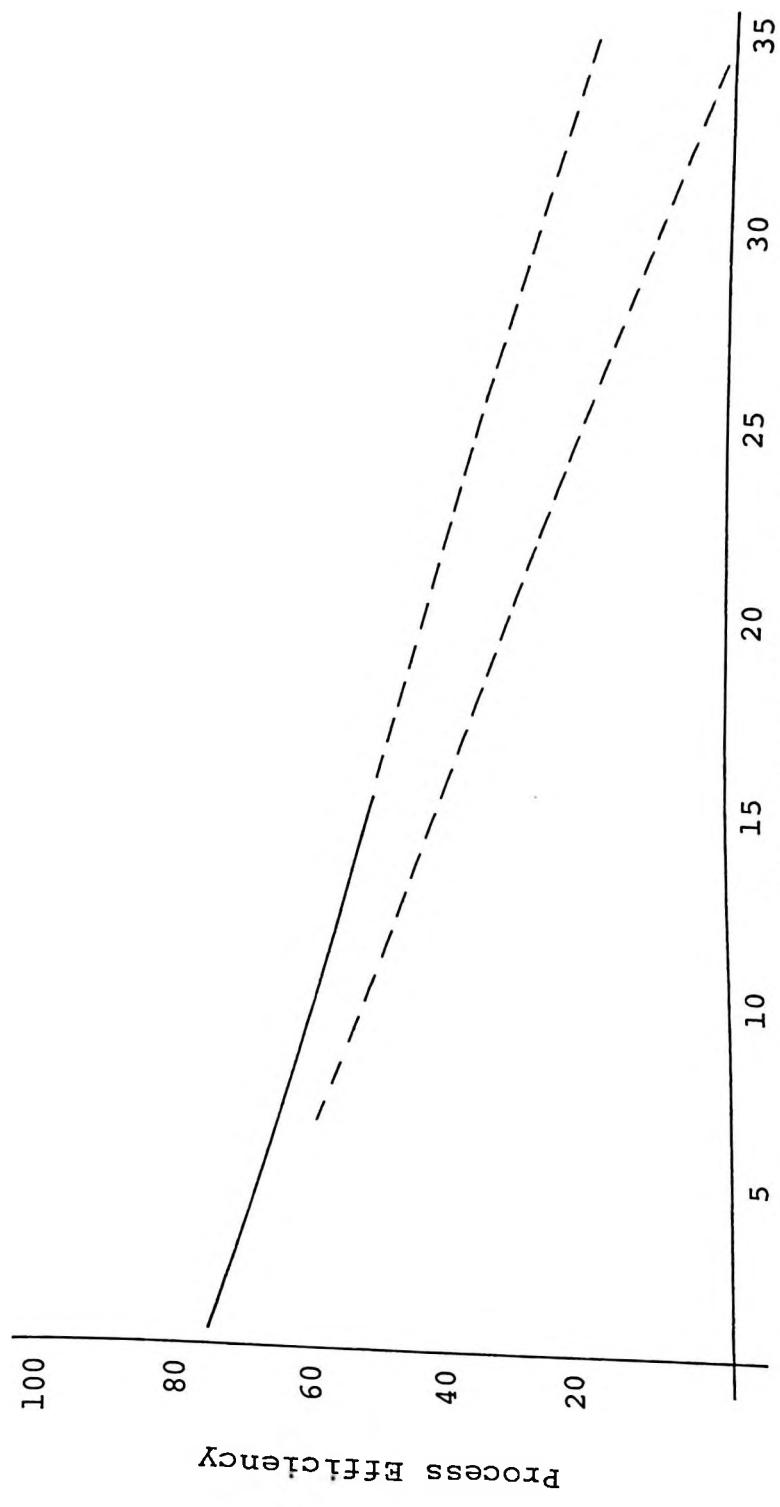


Figure 8 - The Effect of Silica on Pidgeon Process Efficiency

per cent.

$$\frac{79\% - 55\%}{\text{efficiency}} = \frac{14\% - 0\%}{34.04}, \text{ efficiency equals}$$

$$58.3\%$$

$$79.0\% - 58.3\% = 20.7\%$$

That this value is much greater than the 1.5 per cent seen in the tests indicates that silica depresses the reaction greatly when it is present in large quantities. This displays more appreciable effect than Pidgeon envisaged, but his work was with dolomite which has rather large aggregations of silica in the form of quartz or simple silicates. The blast furnace slag possesses the silica in the form of complex calcium-magnesium silicates and calcium-aluminum silicates which are widely dispersed throughout the slag.

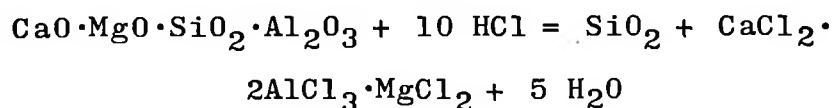
Low yields seem to be a plague of the Pidgeon process with raw blast furnace slag as a feed. The only way to increase the yields appears to be with the removal of silica from the slag.

Method of Removing Silica from Blast Furnace Slag

The removal of silica from the complex silicate is a very difficult problem in chemistry. While it would be quite handy to precipitate the calcium oxide and the magnesium oxide from the slag (remembering that the calcium oxide must be present along with the magnesium oxide to have proper reactions in the

Pidgeon process), this precipitation has not been accomplished. The only known means of separating the magnesium oxide and the calcium oxide from the slag constituents is by the manner used in the chemical analysis of slag (12),(13); this analysis is performed in the following manner. To 0.25 gram of a carefully weighed sample of minus 100 mesh slag add a few mils of water and heat to an incipient boil. Add to the boiling mixture 30 mils of concentrated hydrochloric acid; cover; and bring to a boil. Continue to boil after the hydrochloric acid fumes appear for several minutes or until the volume reaches 6 to 8 mils. Then cool the item for a few minutes. Take up with about 20 mils of hot water, stir to redissolve the soluble salts and filter by gravity through a high grade filter paper. The filtrate left by the operation represents the silica in the slag (13).

The reaction described probably occurs in the following manner

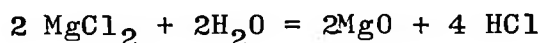


with the silica being filtered out and the chlorides being left in solution with the water.

The solution can now be brought to a boil in an attempt to obtain anhydrous $\text{MgCl}_2 \cdot \text{CaCl}_2 \cdot 2\text{AlCl}_3$.

It is well established that the dehydration of magnesium chloride cannot be accomplished without the risk of decomposition into the oxide and hydrochloric acid. Great care must be exercised here, but with a controlled process, this step can be accomplished.

With the sample in the form of chlorides, it would be possible to convert them back to the oxide form by heating the chlorides in a stream of moist air or flue gas (14). The overall reaction is probably in accordance with this formula for magnesium only



This feed would give a much greater yield in the Pidgeon process, but a study of the economics involved displays very detrimental features. Consider the amount of hydrochloric acid involved in this operation; it would take 14.4 gallons of hydrochloric acid for each pound of slag. The price of hydrochloric acid when bought in large quantities of industrial quality is \$22.50 per ton (15); this type of hydrochloric acid weighs approximately 8.5 pounds per gallon. This value displays a price of \$1.38 for the hydrochloric acid for each pound of slag. Slag contains only 13.58 per cent of magnesium oxide; this percentage indicates a cost of \$10.15 per pound of magnesium oxide. This figure

leads to a cost of \$13.53 per pound of contained magnesium.

Obviously, since magnesium costs only \$0.36 per pound on the American market (1), this method of beneficiating the blast furnace slag cannot be considered as an industrial endeavor. Even with a regeneration system and the use of the residues, this system would not be economical. Combined with this is the difficulty involved in the dehydration phase.

CHAPTER VI

CONCLUSIONS

The following conclusions are based on the results obtained in this investigation:

1. Magnesium can be extracted from blast furnace slag by the Pidgeon process.
2. The yields or efficiencies of the Pidgeon process with blast furnace slag as feed were approximately 1-1/2 per cent.
3. The low yields were probably caused by the large percentage of silica in the blast furnace slag.
4. It appears to be quite difficult to alter blast furnace slag in such a manner so as to produce a more suitable feed for the Pidgeon process. While it is possible to remove the silica from the blast furnace slag by chemical action, the method is far too costly for commercial use.

CHAPTER VII

RECOMMENDATIONS FOR FUTURE INVESTIGATION

The following recommendations are presented concerning future investigation:

1. Mixtures of blast furnace slag and dolomite should be used as feed for the Pidgeon process. It is possible that proper proportions of slag and dolomite would be an excellent feed for the process.
2. Blast furnace slag and free lime should be used as feed for the Pidgeon process. The free lime could compensate for the excessive amounts of silica in the slag.
3. A method should be found that would remove the silica from blast furnace slag in a convenient manner.

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