RI 7719

Bureau of Mines Report of Investigations/1973

Conversion of Ilmenite to Rutile by a Carbonyl Process

UNITED STATES DEPARTMENT OF THE INTERIOR

BIBLIOGRAPHIC DATA SHEET	1. Report No. BuMines RI 7719	2.	3. Recipient's Accession No. PB-214780
4. Title and Subtitle: Conversion of Ilmenite to Rutile by a Carbonyl Process			5. Report Date: January 1973 6. Performing Organization Code
7. Author(s): A. Visnapuu, B. C. Marek, and J. W. Jensen			8. Performing Organization Rept. No.
9. Performing Organization Name and Address: Rolla Metallurgy Research Center, Bureau of Mines, USDI, P.O. Box 280, Rolla, MO 65401			10. Project/Task/Work Unit No. 11. Contract/Grant No.
12. Sponsoring Agency Name and Address: Division of Metallurgy, Bureau of Mines, U.S. Department of the Interior, Washington, DC 20240			13. Type of Report & Period Covered: Research 14. Sponsoring Agency Code
15. Supplementary Notes			

16. Abstracts

The report describes a new carbonyl method for producing synthetic rutile from ilmenite concentrates. Reduced ilmenite is treated with pressurized carbon monoxide to convert the metallic iron to iron pentacarbonyl. The pentacarbonyl is removed, either as a liquid or vapor, leaving a synthetic rutile product. The iron pentacarbonyl can be decomposed to produce high-purity iron, and the carbon monoxide recycled.

17. Key Words and Document Analysis. 17a. Descriptors

Ilmenite
Synthetic rutile
Carbonylation
Carbon monoxide
Iron pentacarbonyl
Metallurgy

17b. Identifiers/Open-Ended Terms

17c. COSATI Field/Group 11F

18. Distribution Statement: Release unlimited by NTIS.

19. Security Class (This Report) UNCLASSIFIED — 21. No. of Pages 20

20. Security Class (This Page) UNCLASSIFIED — 22. Price $3.00

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Report of Investigations 7719

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UNITED STATES DEPARTMENT OF THE INTERIOR
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BUREAU OF MINES
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This publication has been cataloged as follows:

Visnapuu, Aarne

Conversion of ilmenite to rutile by a carbonyl process, by A. Visnapuu, B. C. Marek, and J. W. Jensen. [Washington] U.S. Dept. of the Interior, Bureau of Mines [1973]

20 p. illus., tables. (U.S. Bureau of Mines. Report of investigations 7719)

Includes bibliography.

1. Ilmenite. 2. Titanium dioxide. I. Marek, B. C., jt. auth. II. Jensen, James W., jt. auth. III. Title. IV. Title: Carbonyl process. (Series)

TN23.U7 no. 7719 622.06173

U.S. Dept. of the Int. Library

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CONVERSION OF ILMENITE TO RUTILE BY A CARBONYL PROCESS

by

A. Visnapuu,[1] B. C. Marek,[2] and J. W. Jensen[3]

ABSTRACT

High-grade synthetic rutile has been produced in the laboratory from domestic ilmenite concentrates by a new carbonyl process. The ilmenite was first reduced to convert the iron oxides to metal and then treated at temperatures over 100° C in high-pressure carbon monoxide (CO) to convert the iron to the pentacarbonyl. Rapid carbonylation was achieved in the presence of small quantities of selected promoters. Maximum iron removal occurred at temperatures between 110° and 130° C at CO pressures from 1,000 to 1,400 psig. Iron pentacarbonyl appeared as liquid and vapor in the reactor and could be removed by gravity flow and vapor transport. More than 90 pct of the iron was extracted in 2-hr experiments at pressures of 1,000 psig and above. The TiO_2 product is porous owing to the removal of the iron, has the rutile crystal structure, and is suitable for chlorination. Waste disposal problems associated with the process would be minimal because the iron pentacarbonyl can be decomposed to produce iron powder or pellets for sale and CO for recycling.

INTRODUCTION

Rutile is the preferred material for the production of pigment-grade TiO_2, welding-rod coatings, and titanium metal. The United States does not produce rutile in significant quantity, yet this country consumed 44.9 pct of the world rutile production of 414,429 short tons in 1969 (2).[4] Australia is the principal producer of rutile, followed by Sierra Leone, India, Ceylon, and Brazil. There are small reserves of rutile in this country, but ilmenite is abundant.

A number of methods have been proposed for the production of synthetic rutile from ilmenite. Henn and Barclay (5) classified them into 10 general processes employing (1) caustic or alkali metal salts; (2) solvent extraction; (3) ferric salt leaching; (4) sulfur, sulfides, or sulfates; (5) sulfuric acid; (6) hydrogen chloride gas; (7) hydrochloric acid; (8) solid-state

[1]Research physicist.
[2]Physicist.
[3]Supervisory research physicist.
[4]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

reduction of iron to metal; (9) reduction of iron to metal under slagging conditions; and (10) chlorination techniques.

The more successful processes generally employ solid-state reduction of the iron followed by chemical treatment (11). Often reduction is preceded by an oxidizing roast to convert the iron to the ferric state. The Murso process (12) consists of oxidation and partial reduction under fluidizing conditions followed by hydrochloric acid leaching, which produces a ferrous chloride liquor and upgraded ilmenite. In the Isihara Sangyo process (11), sulfuric acid is used to leach out the iron and iron oxide. In the Becher process (11), the reduced iron is removed by an accelerated rusting process in slightly acidified water. The Summit process (11) leaches the reduced ilmenite with an aqueous solution of ferric salts and regenerates the leached solution. The approximate TiO_2 content of the rutile substitutes produced by these methods ranges from 90 to 95 pct. Although the methods have been developed rather extensively, commercial progress of the synthetic rutile concept has been slow (11).

Since 1958, the Quebec Iron and Titanium Corp. has been producing slag containing 70 to 72 pct TiO_2 by an arc furnace smelting technique (11). The slag is marketed to titanium pigment manufacturers employing the sulfate process but is not suitable as a chlorination feed. The coproduct, pig iron, is of acceptable quality and is marketable.

This report presents the results of a laboratory feasibility study to produce synthetic rutile by a new approach--the reaction of CO with reduced ilmenite to form volatile iron pentacarbonyl, leaving titanium dioxide as a residue. The reaction is as follows:

$$FeTiO_2 + 5\ CO_{(g)} \rightarrow TiO_2 + Fe(CO)_{5\,(g)}.$$

This technique was first proposed by Cochran and Starliper, who demonstrated that up to 95 pct of the iron can be extracted from ilmenite by carbonylation over an extended period of time (1). The present study sought methods for enhancing the rate of formation of iron pentacarbonyl sufficiently to warrant consideration of the process for commercial production of rutile.

A number of extractive processes based on the formation of metal carbonyls have been investigated or are in use. Nickel of high purity has been produced by the Mond process for 70 years, and more recently, the Inco Pressure Carbonyl process has been developed to permit simultaneous extraction of nickel, cobalt, and iron from mineral concentrates and metallurgical intermediates (9). Lewis, Cookston, Coffer, and Stephens (6) investigated the recovery of nickel and iron from lateritic ores. They recovered over 90 pct of the nickel and nearly 90 pct of the iron by carbonylation in the temperature range 110° to 130° C using small additions of NH_3 to the CO to improve recovery. Rhee (10) found best conversion at 121° C for reduced iron ore flotation tailings. Dufour-Berte and Pasero (3) used a fluidized bed reactor for reduction of iron oxide with hydrogen and subsequent carbonyl formation; they varied the temperature between 150° and 170° C and pressures between 25 and 100 atm. Okamura,

Kazima, and Masuda (8) reported 180° C as the optimum temperature for carbonylation of reduced iron oxides at 200 atm and 130° C as the optimum temperature at 100 atm. Mond and Wallis (7) reported that 200° C is optimum for all pressures between 100 and 300 atm.

Common to all the carbonyl processes is the need to catalyze the reaction. Sulfur and sulfur-containing compounds have been favored. Queneau, O'Neill, Illis, and Warner (9) stated that were it not for the increase in reaction rate effected by catalysis, commercial extraction of nickel and iron as carbonyls from reduced metals probably would not be practical.

Althouth the mechanism by which sulfide ions activate the iron surface and make it reactive with CO is not precisely known, there is evidence that no more than a monolayer of iron sulfide is involved. Queneau, O'Neill, Illis, and Warner (9) reported that up to a monolayer of the treated metal surface was composed of metal and sulfide ions approximating the crystal habit and stoichiometry of the most stable sulfide. They theorized that activation was the result of interference with normal bonds existing on a clean metal surface, thereby producing atoms that are nearly free. In the presence of adsorbed CO, such atoms form an activated metal-CO complex, which then builds up into the metal carbonyl. The surface remains uniformly active throughout the volatilization by continuously remaking the sulfide-metal bonds ruptured when metal atoms are removed from the surface. According to Heineke, Bock, and Harenz (4), a set of intermediary metal carbonyl sulfides are formed that lower the apparent activation energy of the carbonyl formation. In either case a very small amount of sulfur is required, and excess sulfur hinders the reaction.

EXPERIMENTAL PROCEDURE

The major part of this investigation consisted of 2-hr carbonylation tests of 10-g samples of prereduced ilmenite in a pressurized reactor. These tests were to determine the effects of temperature, CO pressure, CO flow rate, and selected promoters on the total iron extracted from the charge. After optimum conditions had been established for virtual completion of the reaction in 2 hr, identical procedures were employed on seven different domestic ilmenite samples. Larger samples (ranging up to 280 g in size) were also tested and alternative ways to promote the carbonyl reaction were sought.

Carbonylation of the 10-g samples of reduced ilmenite concentrates was carried out in an Aminco[5] chrome-vanadium steel high-pressure-reaction vessel with an inside diameter of 3.2 cm, a depth of 25.4 cm, and a nominal volume of 200 cm^3. The vessel was heated by an electrical heating shell, and temperature was measured by a Chromel-Alumel thermocouple in a well extending into the center of the reactor. Commercial CO was supplied through a high-pressure regulator. The gas was admitted and passed out through connections in the removable reactor head, and the flow was regulated by a valve at the exit. A precision bore rotameter downstream from the exit valve measured the gas flow.

[5]Reference to specific equipment is made for identification only and does not imply endorsement by the Bureau of Mines.

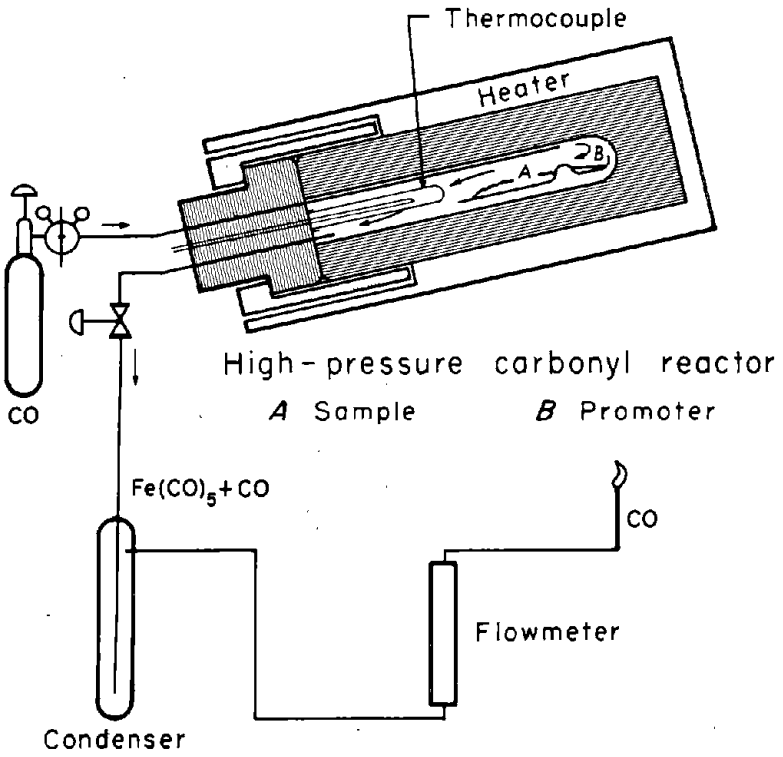

FIGURE 1. - High-Pressure Carbonyl Reactor.

No stirring or shaking mechanism was used. When it was found that liquid $Fe(CO)_5$ accumulated in the reactor, the reactor was tilted 15° from horizontal to allow any liquid to flow away from the sample. The liquid was collected in a trap just beyond the valve. Figure 1 is a schematic diagram of the experimental apparatus.

The sample container was a 12.5-cm semicircular Vycor boat divided by a partition into two compartments: A 10-cm sample compartment open at one end and a 2.5-cm closed compartment that could be used for either liquid or solid promoter. This allowed the sample to be inserted in the reactor in several ways: Simultaneously with a liquid or solid promoter but not in contact; mixed with the liquid or solid promoter; and alone with no promoter. In addition, a gaseous promoter could be added after the reactor was sealed but before pressurization with CO. The boat was positioned open end down. The reactor was maintained at the desired temperature between experiments, and the charge was loaded into the heated reactor. Duration of the experiment was measured from the time the reactor attained the desired pressure to the time depressurization was started. Unless otherwise stated, a CO flow rate of 150 cm^3/min was used. Larger samples of 70 to 280 g were treated in a 1.4-l reactor similar to that shown in figure 1 but with a gas inlet at the rear. Sample containers of stainless steel sheet, or 200-mesh screen, and promoter containers of glass were used in the large reactor.

Domestic ilmenites from seven different geographic locations were investigated. Table 1 shows the particle size distribution of the concentrates. They were of two general types: (1) Ilmenite sands, characterized by rounded particles, and (2) crushed rock with irregular particle shape. Ilmenites A, B, E, and G were sands, and C, D, and F were crushed rock. The crushed rock contained more iron than did the sands.

The concentrates were reduced in a quartz tube furnace. The charge was heated to ~900° C under a flow of helium, reduced with hydrogen for 2 to 4 hr, and cooled to room temperature under helium. It was necessary to oxidize two of the crushed rock ilmenites beforehand to effect complete reduction. The TiO_2 and total iron contents of the ilmenite concentrates before and after reduction are given in table 2.

TABLE 1. - Particle size distribution in ilmenite concentrates

Mesh	Size distribution, pct						
	A	B	C	D	E	F	G
Plus 48.....	0.3	2.4	79.9	21.8	1.8	0.6	0.0
Minus 48 plus 65...	20.5	11.6	15.2	14.1	10.5	7.0	.0
Minus 65 plus 80...	22.4	15.9	2.4	5.8	9.5	6.2	.4
Minus 80 plus 100..	31.9	26.1	1.5	9.2	28.5	14.8	2.5
Minus 100 plus 150.	20.5	35.0	.8	10.4	43.6	29.2	60.9
Minus 150 plus 200.	3.8	6.4	.1	8.4	5.7	19.4	34.0
Minus 200.....	.6	2.6	.1	30.3	.4	22.8	2.2
Total.....	100.0	100.0	100.0	100.0	100.0	100.0	100.0

TABLE 2. - Titanium dioxide and iron contents of the domestic ilmenite concentrates before and after reduction

Concentrate	Ilmenite concentrate composition, pct		Reduced ilmenite concentrate composition, pct	
	TiO_2	Iron	TiO_2	Iron
A	60.2	24.8	68.6	27.5
B	60.9	22.6	69.6	27.5
C	32.5	42.6	40.0	51.5
D	45.8	35.4	51.5	38.1
E	62.6	20.5	71.4	24.0
F	45.6	37.5	53.8	44.3
G	65.0	20.9	74.5	23.1

The amount of iron extracted from the charge was determined by measuring the charge weight loss and by chemical analysis of the depleted charge. Only reduced iron reacted with the CO, so the weight loss was a rapid way to determine the percent of iron conversion. In all experiments to establish the effectiveness of the carbonyl treatment, weight loss was used as the primary criterion, and only a portion of the large number of test samples was analyzed chemically.

Some mass spectrometric analyses were also conducted. An AVCO 90000 series mass spectrometer, described in a previous report (13), was used to analyze the mass numbers of gases emerging from a miniature reactor made from 9/16-in OD, 5/16-in ID high-pressure tubing.

RESULTS

Initial tests were conducted using ammonium polysulfide solution (APS) as the promoter to take advantage of the reported ability of both sulfur (9) and NH_3 (6) to enhance the carbonyl reaction. These indicated that vapors released by APS upon heating, rather than the contact of the APS with the ilmenite, were responsible for promoting rapid carbonylation of the reduced iron. For this reason most experiments to determine the influence of other variables on the carbonyl reaction were conducted using APS that was free to vaporize but not in contact with the sample.

Other significant observations during the initial phases of the investigation, which were incorporated into the subsequent evaluation tests, were the following: (1) The iron pentacarbonyl, $Fe(CO)_5$, formed rapidly as a liquid in the reactor and could be withdrawn into a trap; (2) the flow of CO through the reactor was not essential for carbonyl formation as long as constant pressure was maintained by inflow of CO; (3) grinding the ilmenite concentrate to smaller particle size before reduction did not improve iron extraction; and (4) presence of residual air in the reactor inhibited the carbonylation.

Because of these findings, air was purged from the reactor before each run, the reactor was tilted to allow liquid $Fe(CO)_5$ to flow to an exit tube, and a sample boat open at one end was used to permit liquid to flow from the sample. A CO flow of 150 cm^3/min was usually maintained to carry the gaseous $Fe(CO)_5$ out of the reactor.

Two-Hour Tests on 10-g Samples

Tests to determine iron extraction in 2 hr from 10-g samples as a function of temperature were conducted on reduced ilmenites A, B, and C. Either APS or H_2S was used as a promoter. When APS was used, an amount equal to 8 pct of the weight of the charge was placed in the reactor. The H_2S was used by filling the evacuated reactor with H_2S at atmospheric pressure prior to pressurizing it with CO for a run. The results are presented in figures 2-7, in which iron extracted is plotted against temperature. Results at pressures ranging from 1,000 to 1,600 psig CO and at temperatures of 90° to 150° C are given. From ilmenite A with APS, more than 93 pct of the iron was extracted in some instances, and 90-pct extraction was obtained in nearly half the experiments at temperatures from 110° to 130° C. When H_2S was the promoter, only 85-pct extraction was achieved at best.

Similar data for ilmenite B appear in figures 4-5. With APS catalyst, over 85-pct extraction was obtained at pressures of 1,000 and 1,200 psig, and the useful temperature range appears to extend to 105° C on the lower end. At 1,200 psig, H_2S was a much less effective catalyst than APS.

Ilmenite C is a rock concentrate rather than sand, and for unknown reasons, it responded somewhat better to H_2S promoter than did the others (fig. 7); extraction was about 85 pct. The APS results had more scatter than usual but did exceed 90-pct in some cases (fig. 6).

A limited number of tests at 600 psig indicated that although carbonyl was formed, the amount of iron extracted in a 2-hr period was only one-half or less in comparison with results at pressures of 1,000 psig or higher. On the basis of these observations, it was concluded that CO pressures of 1,000 psig and higher are necessary for rapid formation of $Fe(CO)_5$.

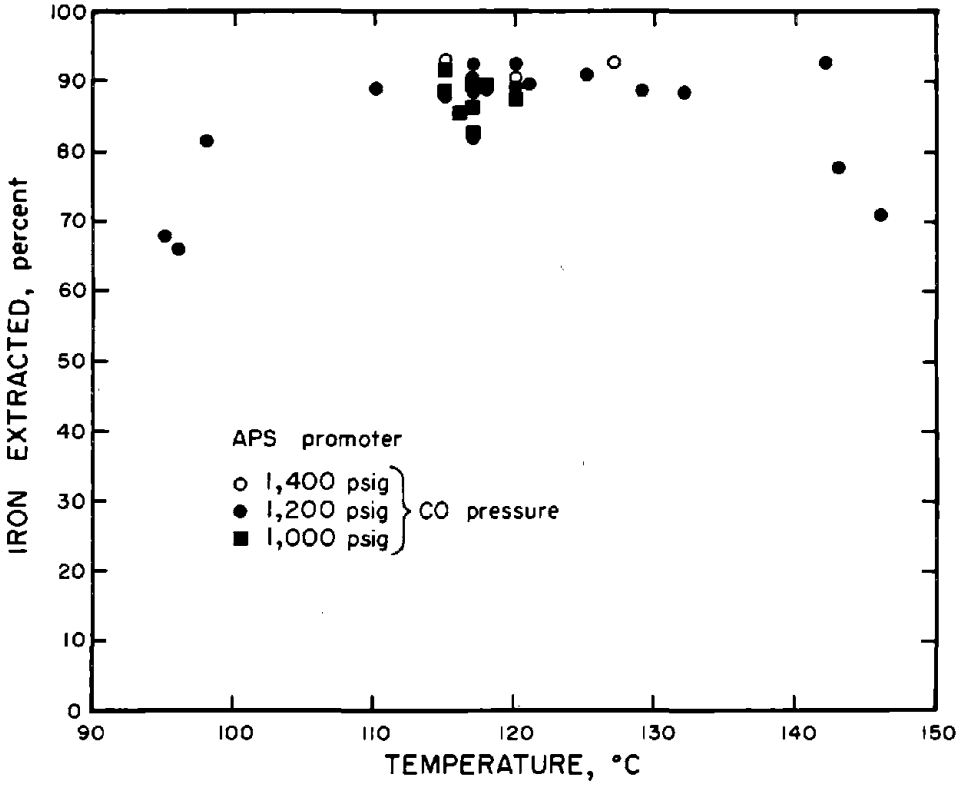

FIGURE 2. - Iron Extraction as a Function of Temperature, Ilmenite A, 2-hr Duration, 150 cm^3/min CO Flow, APS Promoter.

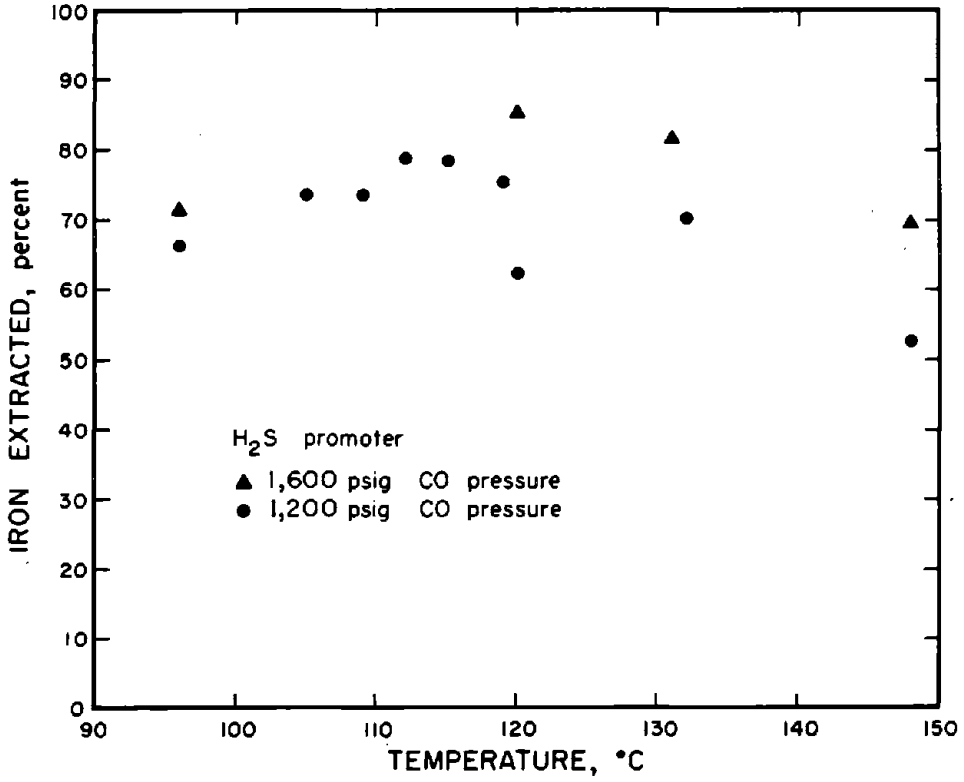

FIGURE 3. - Iron Extraction as a Function of Temperature, Ilmenite A, 2-hr Duration, 150 cm^3/min CO Flow, H_2S Promoter.

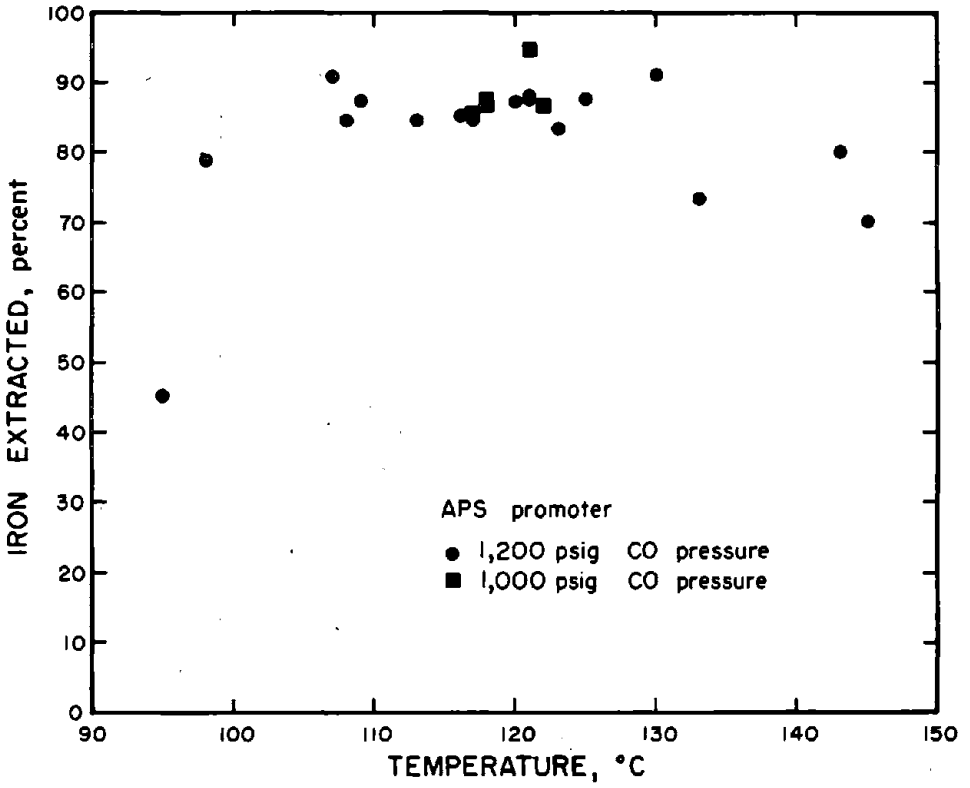

FIGURE 4. - Iron Extraction as a Function of Temperature, Ilmenite B, 2-hr Duration, 150 cm^3/min CO Flow, APS Promoter.

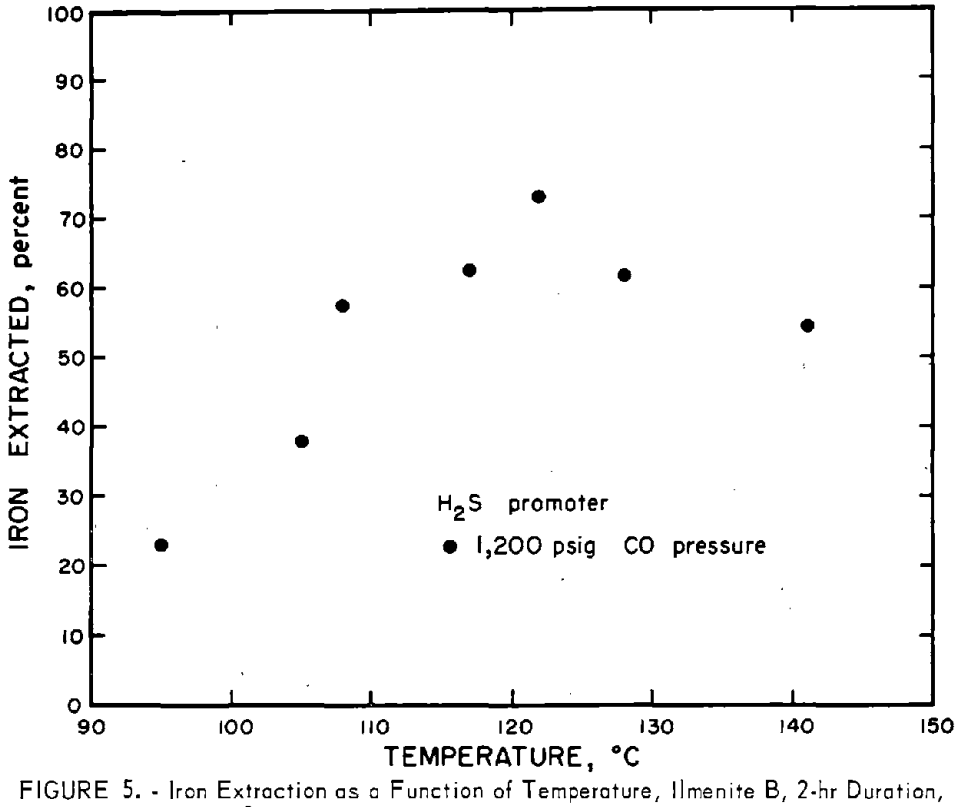

FIGURE 5. - Iron Extraction as a Function of Temperature, Ilmenite B, 2-hr Duration, 150 cm^3/min CO Flow, H_2S Prometer.

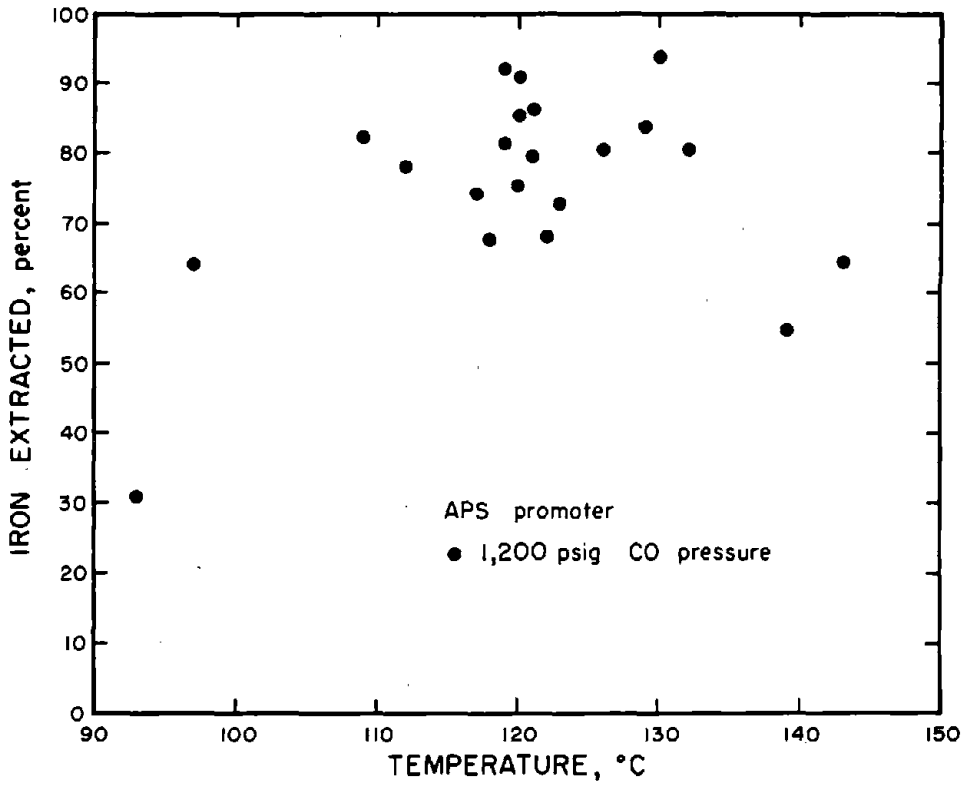

FIGURE 6. - Iron Extraction as a Function of Temperature, Ilmenite C, 2-hr Duration, 150 cm^3/min CO Flow, APS Promoter.

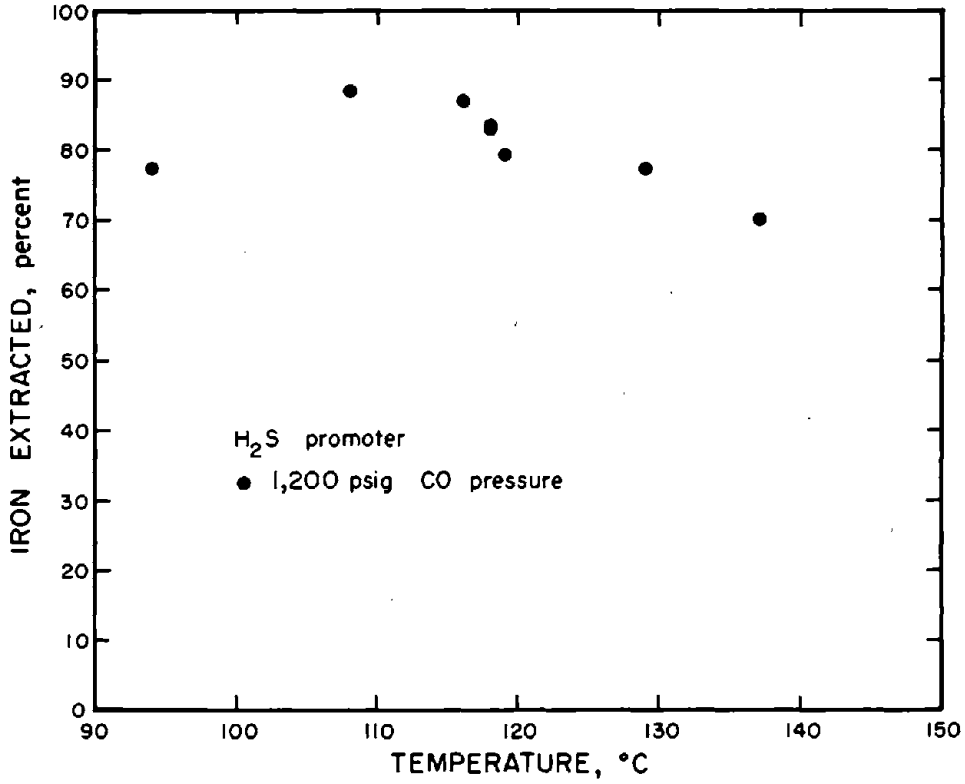

FIGURE 7. - Iron Extraction as a Function of Temperature, Ilmenite C, 2-hr Duration, 150 cm^3/min CO Flow, H_2S Promoter.

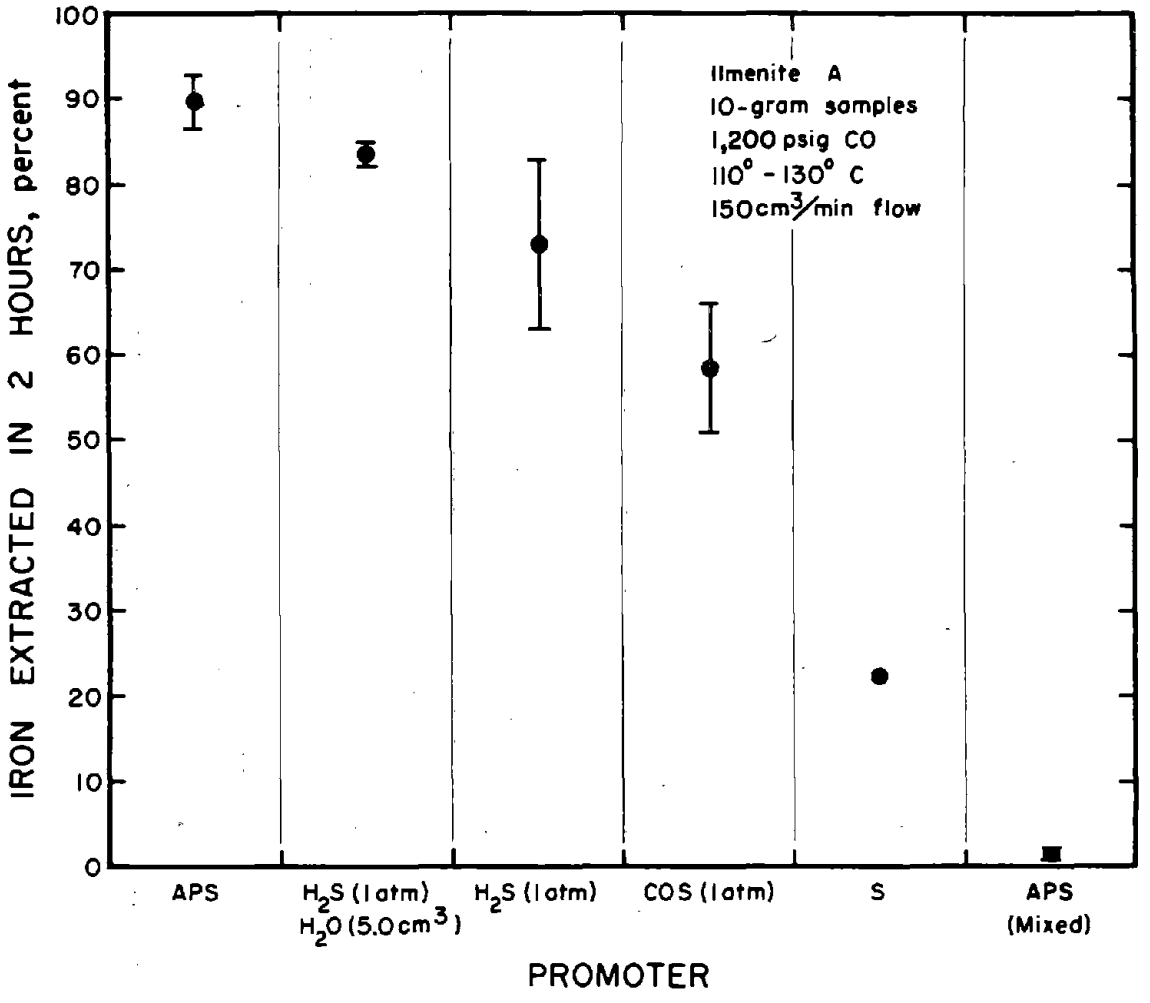

FIGURE 8. - Dependence of Iron Extraction on Selected Promoters.

The effectiveness of various compounds in promoting the carbonyl reaction in reduced ilmenite A is shown in figure 8, based on some of the data presented in table 3. Comparison is made of 2-hr tests in the temperature range 110° to 130° C, 1,200 psig CO pressure, and 150 cm^3/min CO flow rate. Of all the promoters tested, APS, not in contact with the sample, was most effective. The compounds and gases listed in table 3 were selected because they were reported to promote carbonyl formation or represented dissociation products of APS, or both. Since APS dissociates into H_2S, NH_3, H_2O, and residual sulfur, H_2S may be primarily responsible for promoting the carbonyl reaction. Addition of water vapor appears to enhance the catalytic activity of H_2S. Sulfur mixed with ilmenite was not satisfactory. Although only one test with sulfur is shown in the table, it is the best of a series in which the quantity of sulfur mixed with ilmenite was varied. Ammonia, either alone or from the dissociation of $(NH_4)_2CO_3$, was not effective. Mixing APS with the charge resulted in negligible extraction.

TABLE 3. - Dependence of iron extraction on selected promoters

(Ten grams reduced ilmenite A, 1,200 psig CO pressure, 110°-130° C, 2-hr duration, 150 cm^3/min CO flow)

Promoter application			Number of tests	Total iron extracted, pct (by weight loss)
Promoter	Weight, g	Method of application[1]		
APS	0.8	C	13	89.2±2.6
H_2S (1 atm), H_2O	.64	B,C	4	83.3±1.1
H_2S (1 atm)	-	A	3	73.1±9.4
COS (1 atm)	-	A	4	58.2±7.6
Sulfur	.15	D	1	23.2
NH_3 (1 atm)	-	A	1	2.9
$(NH_4)_2CO_3$	.5	E	1	3.3
None	-	A	4	4.7±4.0
APS	.8	E	2	1.8±0.3

[1]Method of application: A, gas applied to evacuated chamber; B, gas applied to chamber; C, liquid in separate compartment of sample boat; D, promoter mixed with sample, chamber evacuated; E, promoter mixed with sample.

The results of experiments under favorable conditions (table 4) show that all seven ilmenites responded to the carbonyl method; iron extractions in a 2-hr period ranged from 80.6 to 94.3 pct. The conditions specified are 10-g samples under CO at 1,200 psig, a set temperature of 120° C that varied less than ±10° C, and activation by APS. The data on iron extraction under "Calculated by weight loss" (table 4) were obtained by weighing each sample before and after carbonyl extraction. Other data shown were obtained from conventional chemical analyses for iron and TiO_2. The samples analyzed chemically were from tests that yielded higher weight losses; thus they are indicative of the better recoveries.

TABLE 4. - Average iron extraction from reduced ilmenite concentrates and composition of synthetic rutile products

(Ten-gram samples under CO g, 1,200 psi, 2 hr at 110°-130° C)

Reduced ilmenite	Iron extraction				Composition of product from chemical analysis	
	Calculated by weight loss, all samples		Calculated by chemical analysis, selected samples			
	Number of tests	Pct extracted	Number of tests	Pct extracted	TiO_2, pct	Iron, pct
A	13	89.2±2.6	4	93.5±3.2	90.3±0.5	2.4±1.2
B	16	87.0±2.5	4	94.3±1.4	91.1±0.8	2.1±0.5
C	17	80.6±7.8	3	91.4±4.0	71.3±2.5	8.0±3.5
D[1]	7	82.0±2.4	5	82.3±3.4	72.3±2.3	9.8±1.9
E	7	90.9±2.5	6	88.8±1.2	89.8±0.4	3.4±0.4
F[1]	6	74.5±5.2	2	80.6±2.6	79.4±1.2	13.3±1.3
G	2	93.5±1.3	2	92.9±0.9	92.6±0.5	2.1±0.3

[1]Oxidized prior to reduction.

Ilmenite sands A, B, E, and G responded similarly to carbonylation. An oxidizing roast prior to reduction did not improve iron extraction, and little was gained from carbonylation in excess of 2 hr. In each case APS was a more effective promoter than H_2S.

Ilmenites D and F differed from the others in response to carbonylation. APS and H_2S were equally effective in promoting the carbonyl reaction, but they required an oxidizing roast prior to reduction and an increased period of carbonylation for best extraction. After 4-hr carbonylation, two samples of ilmenite D averaged 91.6±2.4 pct iron extraction by weight loss and 79.0±5.0 pct TiO_2 by chemical analysis. Sample F of ilmenite carbonylated for 4 hr showed 92.8 pct iron extracted by weight loss and 88.2 pct TiO_2 content.

Figures 9-10 compare the average TiO_2 and iron content of each ilmenite concentrate as received, after reduction, and after 2-hr carbonylation. The graphs combine the data in tables 2 and 4 to show the TiO_2 and iron content after each processing step. Figure 9 shows that the sand concentrates were similar in their original composition and yielded similar synthetic rutile products containing 89.8 to 92.6 pct TiO_2 and 2.1 to 3.4 pct iron. Figure 10 shows that the rock concentrates had a considerably lower initial TiO_2 and higher iron content in comparison with the sands. Like the sands, they were responsive to the carbonyl process and yielded products with greatly increased percentages of TiO_2.

Petrographic analyses of the starting concentrates indicated that in addition to ilmenite they contained small percentages of some of the following: rutile, leucoxene, zircon, quartz, monazite, epidote, tourmaline, garnet, calcite, hornblende, pyrite, and staurolite. These minerals were not reduced by hydrogen, and since the carbonyl process is highly selective in removing only metallic iron, the minerals were found in the final product. The iron remaining in the product is contained in the accessory minerals, possibly in oxides or sulfates formed during carbonylation and, in the case of ilmenites D and F, obviously as unreacted iron. Analysis of three ilmenite A products showed average amounts of the following, in addition to TiO_2 and iron: Sulfur, 0.2 pct; manganese, 1.2 pct; V_2O_5, 3.7 pct; and ZrO_2, 1.8 pct.

Thus, the results of the small-scale tests indicated that with appropriate promoters iron can be extracted rapidly from reduced ilmenite concentrates and recovered as liquid $Fe(CO)_5$, leaving porous TiO_2 as the residue. X-ray diffraction confirmed that the final products had the rutile crystal structure.

Larger Scale Tests

The data in table 3 indicated that the combination of H_2S, H_2O, and NH_3 vapors released by APS in the reactor promoted the carbonyl reaction. Therefore, mixtures of these gases should be just as effective and would be easier to handle than would APS solution in a large-scale application. Experimental work on larger samples of ilmenite A was directed toward development of a mixture of gases that would promote the carbonyl reaction.

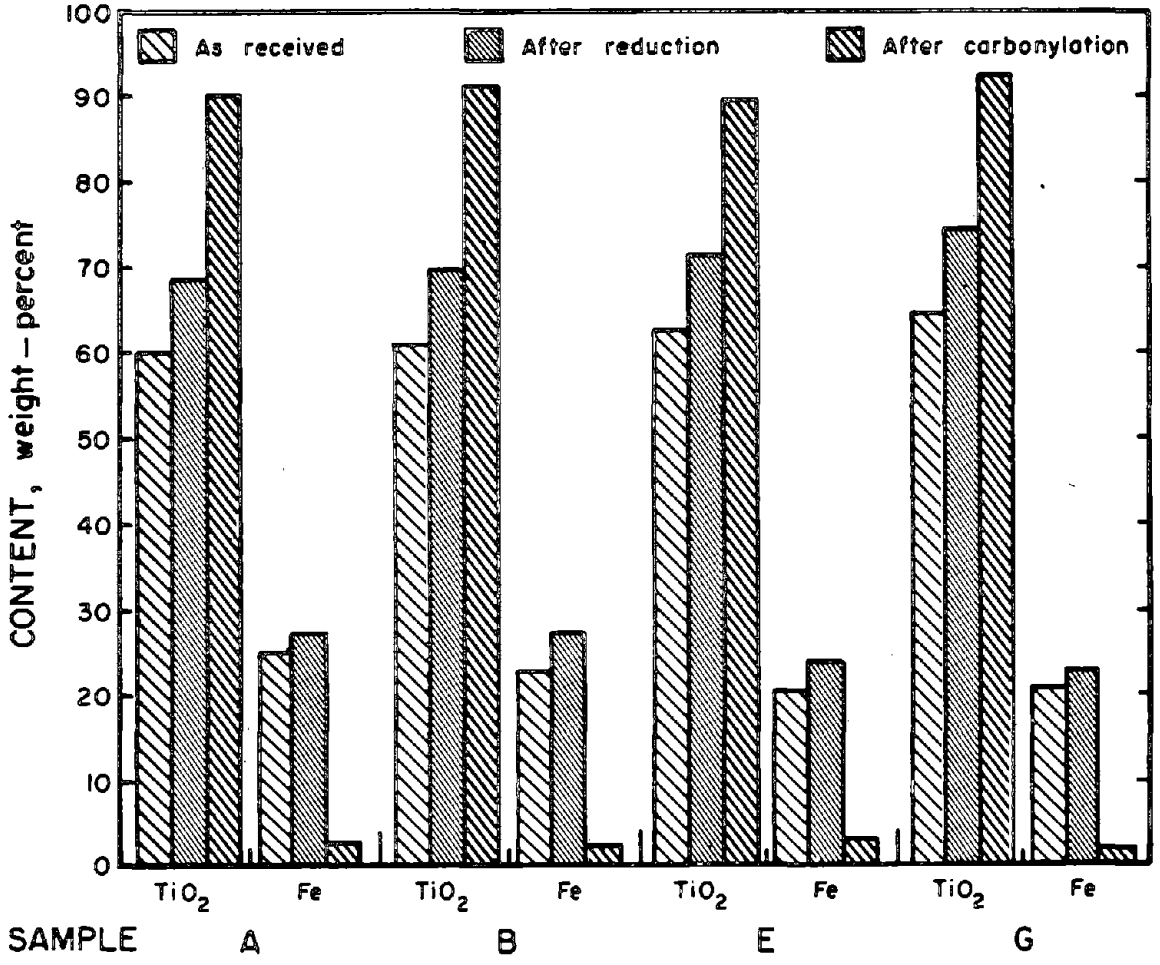

FIGURE 9. - TiO_2 and Iron Contents of Ilmenite Sands.

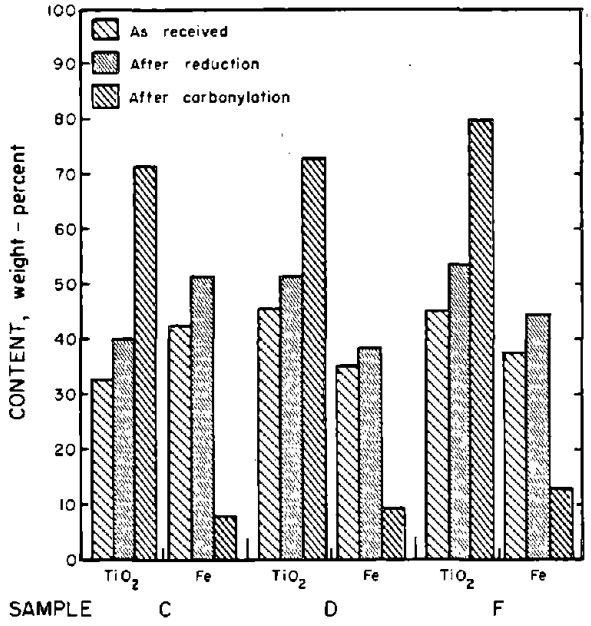

FIGURE 10. - TiO_2 and Iron Contents of Ilmenite Rock.

The scaled-up tests were conducted in a high-pressure reactor similar to that used previously but with a sevenfold increase in volume. Increasing the sample size and quantity of promoter in proportion to the volume resulted in decreased iron recovery. This was especially marked with APS, where recoveries were 50 pct or less of those realized previously. The apparent reason was that the vapors did not diffuse readily into the more tightly packed charge. This was partially verified when use of H_2S and H_2O as promoters increased the iron conversion although the percent iron recovered was less than had been recovered previously. The charge with fewer openings also hindered the flow of liquid $Fe(CO)_5$; an attempt to avoid this was made by fabricating a sample boat of 200-mesh stainless steel screen.

Some results of experiments to extract iron from 70- and 140-g charges in 2 hr using different methods of introducing H_2S, NH_3, and H_2O as promoters are presented in figures 11-14. These are only a portion of the developmental tests. When APS or H_2O was used, the liquid was inserted into the reactor with the charge, but not in contact with it, under a flow of helium. The precharging gas was injected into the sealed reactor at the indicated pressure before pressurization with CO (fig. 11) or mixtures of CO and NH_3 (fig. 12). The mixtures of CO with NH_3 and H_2S, used for data shown in figures 13-14, were fed at 1,200 psig from a pressure vessel in which they had been premixed volumetrically.

One general observation from tests with larger samples was that APS was not as effective a promoter as H_2S. This is shown in figure 11, where iron extraction from 70-g samples in 2 hr using APS, H_2S, and H_2S with H_2O as promoters are compared. When H_2O was introduced with H_2S, as is the case with APS, its effectiveness was even greater. Based on these observations, numerous experiments were conducted to find the most effective way to introduce the gases H_2O, NH_3, H_2S, and CO to extract the iron by carbonylation.

Small quantities of NH_3 mixed in the CO greatly altered the ability of H_2S to promote the carbonyl reaction. Without NH_3, H_2S pressures were not critical. With NH_3, they became critical (fig. 12). Best extraction was at the H_2S precharging pressure of 1/4 atm, and extraction decreased rapidly at lower and higher pressures. A significant point is the increase of iron extraction to 90 pct, which could not be obtained in other experiments without NH_3 mixed in the CO. A mixture of 99.9 vol pct CO and 0.1 vol pct NH_3 was found to be the best.

The amount of H_2S necessary for optimum extraction was dependent on charge weight and indicated that a hydrogen sulfide-to-iron mole ratio of 0.01 was required for optimum extraction.

Figure 13 shows the effect of CO and H_2S concentration ratio on iron extraction using mixtures of these gases and NH_3. Again the importance of controlling the H_2S concentration is apparent. Iron extraction here is not as high as with H_2S precharging, but the results indicate that selected mixtures of the three gases will promote the carbonyl reaction.

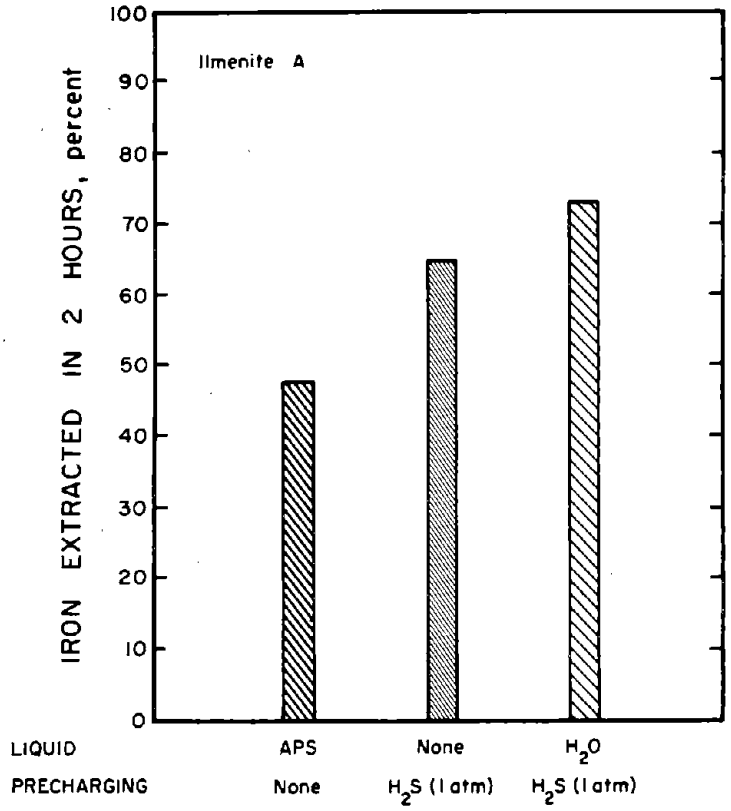

FIGURE 11. - Iron Extraction From 70-g Samples Using APS and H_2S Promoters, CO at 1,200 psig.

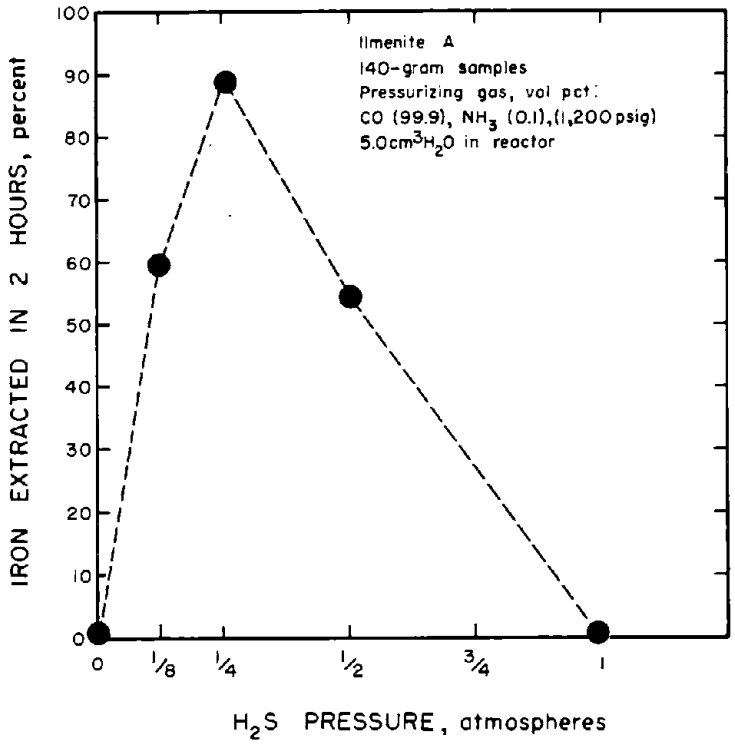

FIGURE 12. - Effect of Concentration of Precharging H_2S on Yield.

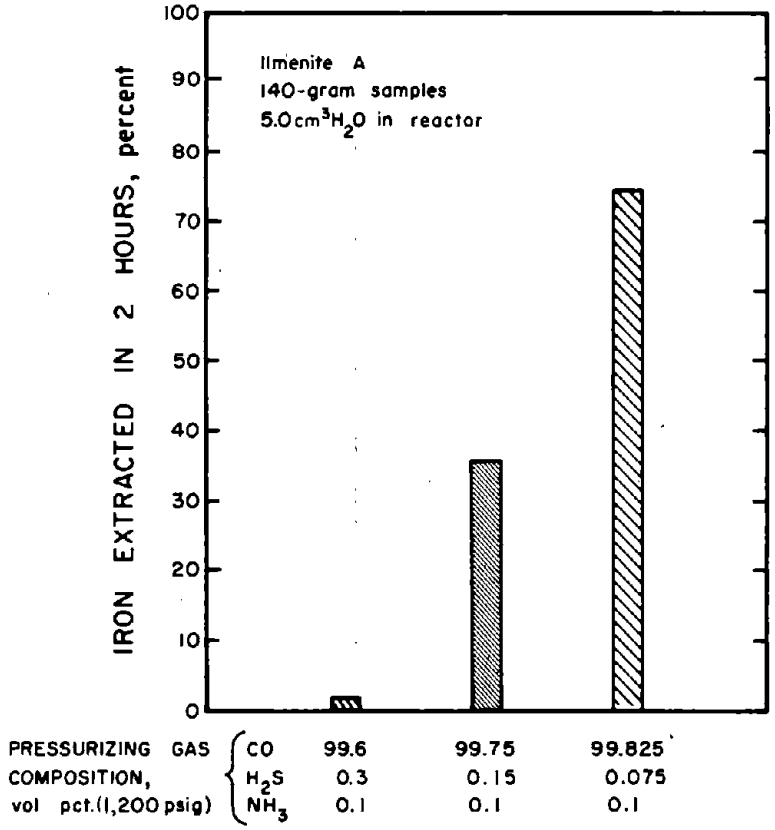

FIGURE 13. - Effect of H_2S Concentration on Yield.

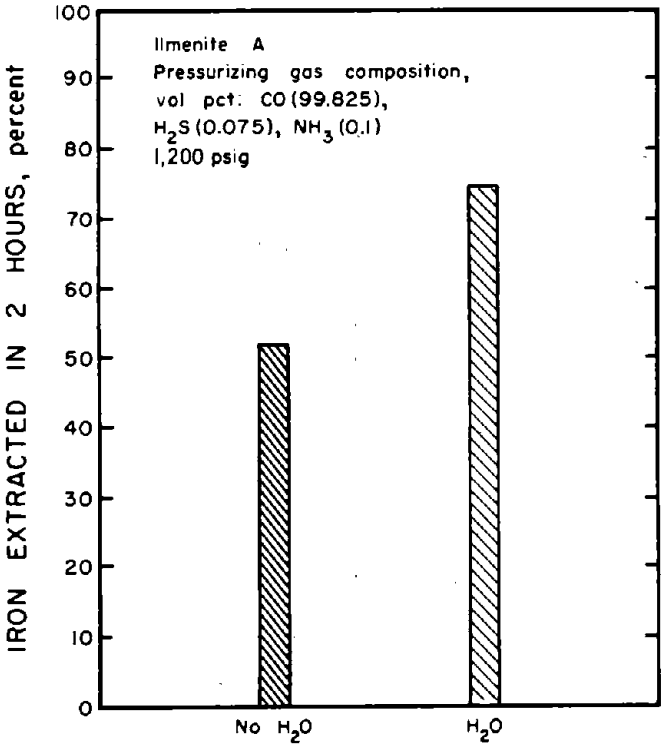

FIGURE 14. - Effect of H_2O Addition on Yield From 140-g Samples.

Figure 14 compares the effect of H_2O addition with the three-gas mixtures. In the presence of H_2O iron extraction improved, but the partial pressure of H_2O was not critical.

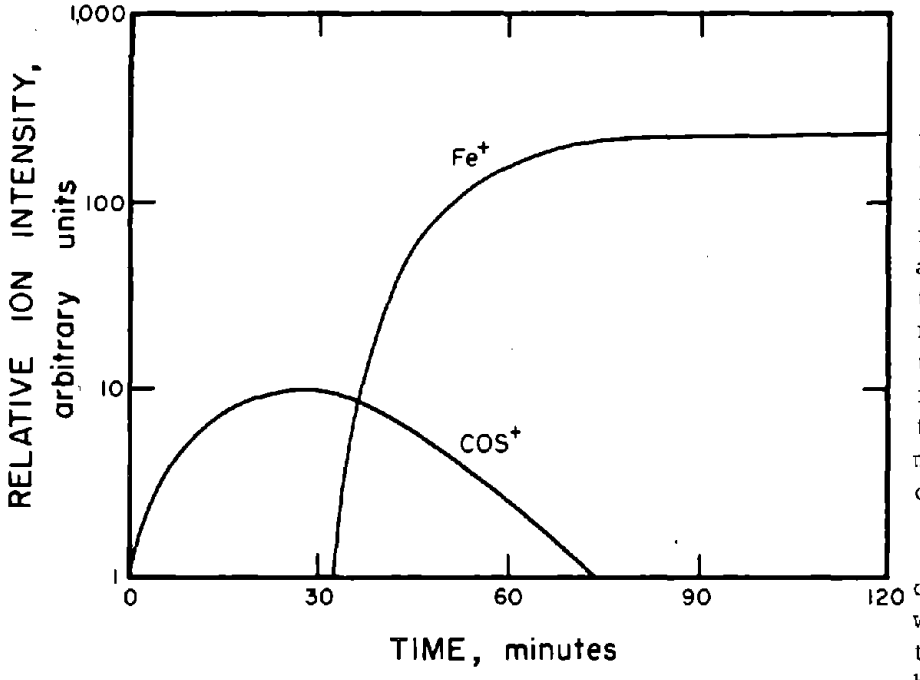

FIGURE 15. - Relative Variation of Fe^+ and COS^+ Ions in CO Flowing Through Miniature Carbonyl Reactor as Determined by Mass Spectrometer.

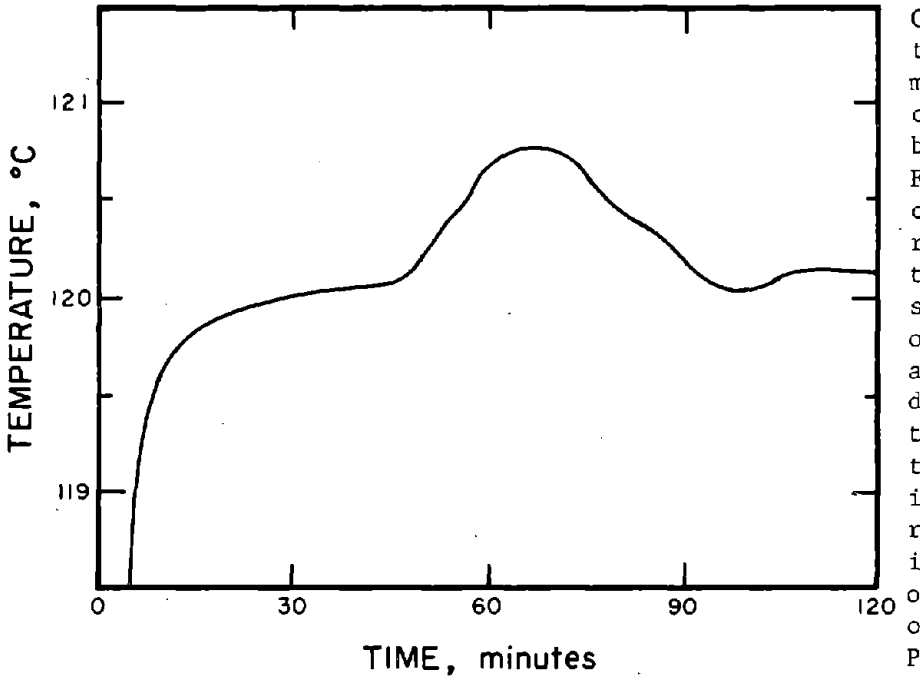

FIGURE 16. - Temperature Record of a Typical 10-g, Ilmenite A Carbonylation Test.

Reaction Studies

A number of mass spectrometric measurements of the CO carrier gas flowing through a miniature carbonyl reactor was performed to analyze the carbonyl reaction. A fraction of the regulated gas flowing from the reactor was admitted into the mass spectrometer through a variable leak for mass analysis as a function of reaction time.

Principal gases detected, other than CO, were $Fe(CO)_5$ and COS when the reaction was promoted by either APS or H_2S. In figure 15 is shown a typical variation in the relative concentration of $Fe(CO)_5$ and COS as a function of reaction time with H_2S as the promoter. Variation of the COS concentration is represented by the ion COS^+, and of $Fe(CO)_5$ by the ion Fe^+. The curves in the graph do not represent the true concentration ratios; rather, they show the relative variation of the ion concentrations as a function of time. Ions due to H_2S were detected at the start of each test, but they vanished rapidly. It is inferred that the H_2S reacts with the reduced iron, is adsorbed, is chemisorbed, or undergoes a combination of these three processes. Presumably, the combination of H_2S with iron involved only surface atoms, since

the mole fraction of H_2S added was always very small compared with the moles of iron present in the charge.

From the initial increase of COS and the absence of $Fe(CO)_5$ in the reactor, it appears that COS was formed by the reaction of CO with the sulfur on the iron surface and that an excess of sulfur for carbonyl formation was present. Formation of COS proceeded until the excess sulfur was removed, and then the formation of $Fe(CO)_5$ started as indicated by the rapid increase of $Fe(CO)_5$ and a gradual decrease of COS (fig. 15).

These observations can be interpreted in accordance with the catalytic function of sulfur in carbonyl iron formation reported by Queneau, O'Neill, Illis, and Warner (9). Sulfur in excess of the monolayer required for activation forms bulk sulfide and is deleterious to the carbonyl reaction. Apparently the observed COS was formed when excess sulfide atoms on the surface reacted with CO; after the excess sulfur was removed, the carbonyl formation began.

Evidence that a time lapse occurred before the start of the carbonyl reaction was also obtained from continuous temperature records of carbonylation tests of 10-g and larger charges. A typical temperature versus time record of a 10-g charge is shown in figure 16. After initial stabilization of temperature, a marked increase in temperature occurred, followed by a decrease to approximately the previous level. The increase in temperature after 45 min corresponded to the observed flow of liquid $Fe(CO)_5$ from the reactor, indicating rapid formation of the compound by the exothermic reaction. This record was selected to correlate with figure 15. In runs that gave maximum yields, the time lapse was shorter, and the temperature increase and formation of liquid $Fe(CO)_5$ were observed earlier.

DISCUSSION

Carbonyl processes have been applied commercially to recover and purify iron and nickel. The carbonyl method can also extract iron from reduced ilmenite to produce a synthetic rutile and high-purity iron. Under optimum conditions of temperature, CO pressure, and promoter, the reaction is rapid and nearly all the reduced iron is extracted as $Fe(CO)_5$. Selection of the promoter and the method by which it is applied are of prime importance in initiating and sustaining the reaction. In tests with 10-g charges, APS was found to be the best promoter, whereas in scaled-up charges, combinations of H_2S, H_2O, and NH_3 were more effective. The fact that the effectiveness of APS as a promoter decreased in scaled-up experiments does not preclude its use as a promoter in large-scale ilmenite upgrading processes although gaseous combinations of H_2S, H_2O, and NH_3 may be easier to use from a technological standpoint.

The carbonyl process differs from the more conventional methods of ilmenite upgrading in that high-pressure CO is used to extract the iron. High-pressure carbonylation processes that appear to be adaptable to the extraction of iron from reduced ilmenite are in operation at the present time. For example, the International Nickel Co. has developed a high-pressure carbonyl

method, designated as the Inco Pressure Carbonyl (IPC) process, to extract nickel, iron, and cobalt from specially prepared granular feed (9). The metals are converted to carbonyls in 150-ton-capacity rotary vessels at operating pressures of 70 atm. The mixed metal carbonyls are carried from the reactor by a flow of CO and condensed to be later separated by fractional distillation. The separated distillates are then decomposed to produce high-purity nickel pellets or powder, and iron-nickel powder. A reactor of similar design would meet the basic requirements for extracting iron from reduced ilmenite.

Carbonyl synthetic rutile would eliminate the waste disposal problems encountered in some other ilmenite upgrading processes since the recovered $Fe(CO)_5$ can be decomposed to high-purity byproduct iron and CO. The latter can be recycled. If the iron in powder form is not readily marketable, it could be formed into pellets or briquettes and, under the least favorable contions, could be sold at the price of pig iron or No. 1 scrap.

The TiO_2 content of the synthetic rutile product in this study was partially dependent on the accessory mineral content of the starting ilmenite concentrates. Since the primary objective was to investigate the carbonylation of iron in reduced ilmenite, removal of these accessory minerals was not stressed. However, they could be removed by mineral dressing techniques if necessary. A logical point of removal would be after reduction, where the highly magnetic reduced ilmenite could easily be separated from the other minerals. Pelletizing the reduced ilmenite may increase the rate of carbonyl formation by providing better access of the promoters and CO to the charge.

CONCLUSIONS

On the basis of small-scale laboratory experiments, it is concluded that carbonylation of the iron in reduced ilmenite by treatment with CO at high pressure in the presence of selected catalysts, removal of the iron carbonyl as a liquid or vapor to be decomposed to obtain byproduct iron, and recycling the CO constitutes a viable process for producing synthetic rutile that merits further development. Carbonylation in the presence of appropriate catalysts or promoters, at CO pressures above 1,000 psig, and temperatures in the range 110° to 130° C, proceeds rapidly. The composition, concentration, and method of introduction of the catalytic agents are critical factors in determining the rate and completeness of the iron extraction.

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