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Recovery of Manganese From Steel Plant Slag by Carbamate Leaching

By Synthia N. McIntosh and Elizabeth G. Baglin

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mg/L	milligram per liter
g	gram	min	minute
h	hour	mL	milliliter
in	inch	μm	micrometer
kW	kilowatt	mol	mole
L/min	liter per minute	pct	percent
lb/st	pound per short ton	st	short ton

RECOVERY OF MANGANESE FROM STEEL PLANT SLAG BY CARBAMATE LEACHING

By Synthia N. McIntosh[1] and Elizabeth G. Baglin[2]

ABSTRACT

The U.S. Bureau of Mines investigated the feasibility of using ammonium carbamate ($NH_2CO_2NH_4$) leaching to recover manganese from steel plant slag. This investigation showed that treatment of the slag in hydrogen prior to leaching enhanced manganese extraction. Up to 80 pct of the manganese and 50 pct of the iron could be extracted from a silicon steel slag that had been pretreated in hydrogen at 700° C. Two 4-h leaching stages conducted at ambient temperature with a solution containing ammonia and carbon dioxide dissolved manganese and iron as their carbamate complexes. Heating the pregnant solution to 65° to 85° C decomposed the complexes and precipitated the metals as insoluble carbonate salts. Ammonium carbamate leaching of other slags from several steelmaking plants produced lower manganese extractions, which suggests that the method cannot be applied satisfactorily to all steelmaking slags.

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INTRODUCTION

Manganese is an essential element used in the production of quality steel. It has traditionally been used to perform the vital functions of deoxidization and desulfurization, but it also imparts to steel the alloying properties of strength, toughness, hardness, and hardenability, and it inhibits formation of embrittling grain boundary carbides. For these reasons, the steel industry consumes 90 pct of the manganese used in this country. There is no known replacement for its use in steel.

Presently, the United States is totally dependent on foreign sources to meet its manganese demand. In 1989, 639,000 st of manganese ore, 476,000 st of ferromanganese, and 255,000 st of silicomanganese were imported, principally from the Republic of South Africa, France, Brazil, Gabon, Australia, and Mexico. The United States produced 99.1 million st of raw steel and steel castings, and the unit manganese consumption averaged 8.1 lb/st steel (*1*).[3]

The United States does not have any economically significant high-grade manganese deposits and no practical method of recovery exists for its low-grade deposits. For an ore reserve to be economically significant, it must be large, high enough in grade (generally more than 35 pct Mn) and accessible at reasonable cost, and the ore must meet various physical and chemical standards. Unless economical recovery methods are found, the United States will continue to depend on foreign reserves.

There are possible sources of manganese in the United States that could be used if economical recovery methods were found. One source is slag generated during steelmaking. Basic oxygen furnaces (BOF's), which account for approximately 60 pct of raw steel production in the United States (*2*), generate 5 million st of steelmaking slag each year (*3*). A portion of the slag is recycled in the blast furnace to recover the metal and flux values, but recycling is limited because the slag contains phosphorus that builds up excessively in the steel if sufficient slag is not removed from the processing stream. It has been reported that only 40 pct of the BOF steelmaking slag is recycled (*4*). The remaining 60 pct is either sold as construction aggregate or dumped. It is estimated that the steelmaking slags that are not recycled to the blast furnace represent more than 132,000 st of lost manganese per year, or approximately 20 pct of current U.S. manganese consumption. Steelmaking slags present a potential source of manganese and their utilization would help to meet the demand of manganese in the United States if viable methods of recovery could be found.

Prior to 1960, most steel in the United States was produced via the blast furnace and open-hearth furnace route, and the high-silica (SiO_2) slags generated were refractory to hydrometallurgical processing. In the early 1950's, the U.S. Bureau of Mines developed a method to recover manganese from open-hearth slags by a lime (CaO) clinkering and ammonium carbamate ($NH_2CO_2NH_4$) leaching process (*5-6*). Lime was added to the high-silica slag to change the lime-to-silica ratio, and the mixture was roasted at 1,350° C to form a clinker. After hydrogen reduction at 700° C to convert the manganiferous material to manganous oxide, the clinker was leached in a strong ammonia-carbon dioxide solution to dissolve manganese and iron as their carbamate complexes. The metal values were precipitated from the pregnant solution as insoluble carbonate salts by distilling the ammonia out of the solution. A ferromanganese product suitable for use as blast furnace feed was produced by calcining the carbonate mixture.

With the advent of the BOF steelmaking process, the nature of the slags has changed. More lime is added to the flux to control phosphorus and sulfur in the steel. BOF slags are composed primarily of lime and iron oxides and contain an average of 5.7 pct MnO (*7*).

As part of its mission to reduce dependence on foreign sources for critical and strategic minerals, like manganese, the Bureau conducted research to determine whether manganese can be recovered from currently produced BOF slags by ammonium carbamate leaching. The increased amount of lime added to the flux during steelmaking may make BOF slag directly amenable to carbamate leaching without the lime clinkering step that was required in the treatment of open-hearth slags. A flowsheet for the proposed procedure is shown in figure 1.

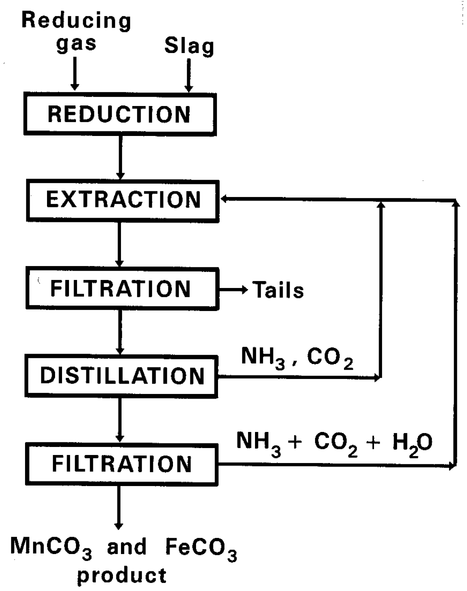

Figure 1.—Flowsheet of proposed process.

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[3] Italic numbers in parentheses refer to items in the list of references at the end of this report.

EXPERIMENTAL PROCEDURES

MATERIALS AND SAMPLE PREPARATION

Slag samples were obtained from several BOF steel plants. They were crushed to minus 1/4 in and the magnetic prills were removed using a permanent magnet held at a distance of 1 in. Splits of the nonmagnetic fractions were ground to the desired mesh size prior to further treatment.

PRETREATMENT OF SAMPLES

Pretreatment of the slag samples was carried out in an alumina tube positioned in a tube furnace. Temperatures were measured using a thermocouple placed in the slag bed. In each test, 50 g of slag was heated to the desired temperature under a flow of helium. When the furnace reached temperature, the gas flow was switched to a chosen reducing or oxidizing gas flowing at a rate of 1.9 L/min during the pretreatment period. Cooling was conducted under a flow of helium.

Early in this work it was discovered that manganese recovery by carbamate leaching decreased about 30 pct when the hydrogen-reduced slag was exposed to air overnight, indicating that reaction(s) inhibiting manganese extraction occurred. To avoid the reaction(s), reduced slag samples were stored either in a vacuum desiccator or under helium until leached. With proper storage, the reproducibility of the ensuing extraction experiments was within ±5 pct.

LEACHING

Leaching tests were conducted at room temperature using 10 to 36 g of ground slag per 100 g of ammonium carbamate solution. The ammonia-to-carbon dioxide mole ratio in the leachant was varied between 3.5 and 7.0 by mixing calculated quantities of solid ammonium carbamate, concentrated ammonium hydroxide (NH_4OH), and water. The reaction vessel was a magnetically stirred 250-mL sealed glass flask. At the completion of each leaching test, the slurry was filtered and displacement washed with 75 mL of fresh leachant followed by 75 mL of water. The slurries filtered easily, but no engineering data were generated.

In multiple-stage extraction tests, the tails were washed only after the last leach. During leaching rate studies, 2.5-mL samples were taken from the slurry every hour and filtered through glass fiber filter paper.

Aliquots of the pregnant solutions were diluted with known amounts of concentrated hydrochloric acid prior to chemical analysis to prevent precipitation of dissolved metals, especially iron, which occurred upon exposure of the ammonium carbamate solutions to the air. The tails and neutralized filtrates were analyzed by inductively coupled plasma spectroscopy.

MANGANESE PRECIPITATION

Solubilized manganese and iron were precipitated from the pregnant solution as carbonate salts when ammonia was removed by heating the solutions to temperatures between 65° and 85° C. Separation of the precipitated carbonates by filtration was conducted under a nitrogen atmosphere. Absence of oxygen during filtration prevented oxidation of ferrous iron to ferric iron, which otherwise would form difficult-to-filter hydrous ferric oxide in the strongly basic leach solution. The carbonate precipitate was air dried at ambient temperature.

RESULTS

CHARACTERIZATION OF SLAG SAMPLES

The chemical analyses of slag samples used in this study are summarized in table 1. Manganese concentrations varied from 0.6 to 5.5 pct. The slags were composed primarily of calcium, iron, magnesium, and silicate compounds.

The slags were characterized by scanning electron microscopy (SEM) and X-ray diffraction analysis to determine grain size and composition of the mineral phases present. The X-ray crystal phase identification results are summarized in table 2. The type and amount of the phases varied considerably from sample to sample. Predominant components included β-dicalcium silicate (β-Ca_2SiO_4), calcium hydroxide [$Ca(OH)_2$], magnesium oxide (MgO), wustite (FeO), and two calcium iron oxide compounds, $Ca_2Fe_2O_5$ and $CaFeO_2$. The manganese content of the slags was too small for the manganese phases to be identified by X-ray diffraction.

Scanning electron microscopy showed that most of the slags exhibited irregularly shaped but relatively large mineral grains. Photomicrographs of two such slag samples are depicted in figures 2*A* and 2*B*. The grains were often larger than 50 μm in size. The darkest phases in the photomicrographs were composed of dicalcium silicate, which contained low concentrations of iron and manganese. Brighter phases contained large amounts of calcium and iron with small concentrations of aluminum, magnesium, manganese, and silicon, or were manganese-rich, iron-magnesium-bearing grains whose composition corresponded roughly to the formula $FeMgO_2$. In addition, white areas composed largely of metallic iron with small amounts of calcium, magnesium, and manganese were sometimes observed. These were obviously steel particles that had not completely separated from the slag during steelmaking. The highest concentrations of manganese resided in the $FeMgO_2$ phase.

Two samples, the carbon steel slag from Indiana Harbor, IN, and one of the carbon steel slags from Warren, OH (C-2), were extremely fine grained, with grains typically less than 5 μm in size. A photomicrograph of the Indiana Harbor slag is shown in figure 2*C*.

The silicon-carbon steel slag from Natrona Heights, PA, exhibited a high proportion of dark silicate grains (fig. 2*D*). Manganese was found only in the silicate phase, and not elsewhere. Brighter particles in this photomicrograph were composed of iron and chromium. The presence of chromium and the fact that the overall manganese content was only 0.6 pct indicate that this slag is probably an alloy-steel slag. The steel mill at Natrona Heights produces both BOF and alloy steels, and it is possible that the slags were mixed in the storage dump from which the sample was collected.

SLAG PRETREATMENT

Experimental procedures were developed using the silicon steel slag from Warren, OH, and then applied to other slag samples.

Reports in the literature indicated that recovery of manganese from open-hearth slags and silicate manganese ores was enhanced if the materials were treated with hydrogen at elevated temperature (*5-6, 8*) before leaching with ammonium carbamate. Preliminary studies showed that manganese extraction from modern silicon steel slag also increased after hydrogen reduction.

Table 1.—Chemical analyses of steel plant slag samples, percent

Location and type of steel	Mn	Fe	MgO	CaO	SiO_2	Al_2O_3	P
East Chicago, IN: Low C ...	5.5	23	9.1	35	14	1.4	0.42
Indiana Harbor, IN: C	2.1	13	7.1	36	13	3.2	.13
Natrona Heights, PA:							
Si-C	.6	12	13.0	28	19	4.0	<.10
Si	1.1	3	9.6	38	37	4.5	<.10
Warren, OH:							
Si	3.0	26	9.8	39	11	1.2	.29
C:							
Sample 1	2.2	16	9.8	32	11	3.8	.11
Sample 2	3.3	21	7.3	39	13	0.9	.20

Table 2.—X-ray analyses of steel plant slag samples by phase number[1]

Location and type of steel	1	2	3	4	5	6	7	8	9	10	11	12	13	14
East Chicago, IN: Low C ..		M						t			t	M		
Indiana Harbor, IN: C				M	t						t		t	m
Natrona Heights, PA:														
Si-C	m		t	M		M	m					t	m	
Si			M							M	M	M		
Warren, OH:														
Si		M									M	M		
C:														
Sample 1		M						m					m	
Sample 2				M	m	M			m	M	m		m	

M Major. m minor. t trace.

[1] Phases are:

1 ...	γ-Ca_2SiO_4	6 ...	MgO	11 ...	$CaFeO_2$
2 ...	β-Ca_2SiO_4	7 ...	$Mg(OH)_2$	12 ...	FeO
3 ...	$Ca_2MgSi_2O_7$	8 ...	SiO_2	13 ...	Fe_3O_4
4 ...	$Ca(OH)_2$	9 ...	C	14 ...	Fe_3C
5 ...	$CaCO_3$	10 ..	$Ca_2Fe_2O_5$		

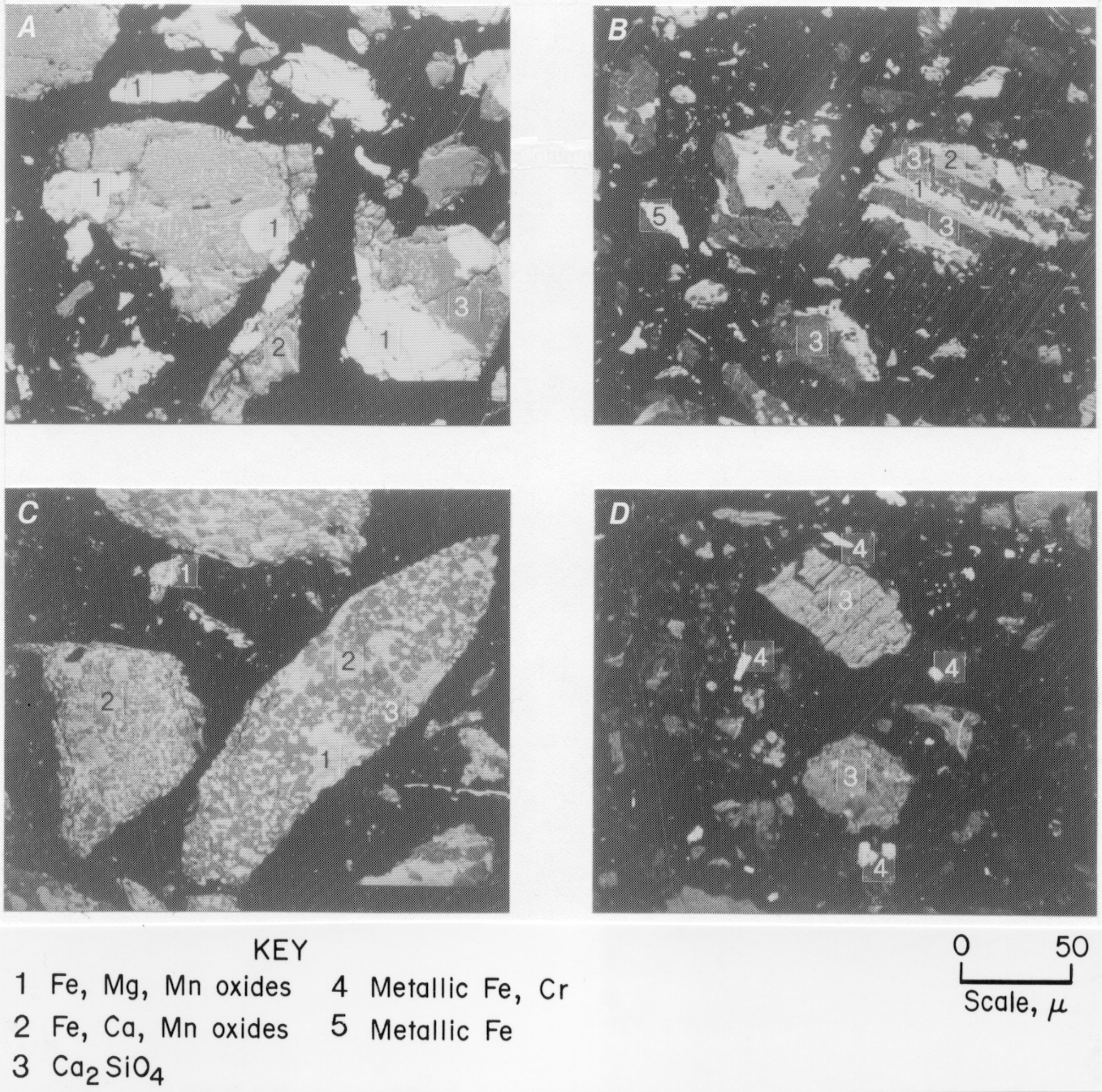

Figure 2.—Scanning electron microscope photomicrographs of four basic oxygen furnace slags. *A*, Warren, OH, silicon steel; *B*, Warren, OH, carbon steel; *C*, Indiana Harbor, IN, carbon steel; *D*, Natrona Heights, PA, silicon-carbon steel.

Hydrogen treatment temperatures from 500° to 800° C were evaluated to determine the optimum temperature for manganese recovery. Minus 100-mesh slag was reduced for 2 h in hydrogen and leached in two stages with ammonium carbamate solution. The leach slurries were composed of 18 g of slag and 100 g of leachant containing a 4.5 mol ratio of ammonia to carbon dioxide. Each leach was conducted for 2 h at ambient temperature. Figure 3 summarizes the results of these tests. The data show that 700° C is the optimum temperature for recovering manganese from the silicon steel slag, with an extraction of 74 pct. Iron exhibits a similar temperature profile with a maximum extraction of 50 pct at 600° C, which decreases slightly to 46 pct at 700° C.

Figure 4 shows that a 2-h reduction period is sufficient to achieve maximum extraction. Hydrogen treatment for more than 2 h did not significantly enhance manganese recovery.

PRETREATMENT WITH OTHER GASES

A number of tests were performed to determine whether gases other than hydrogen could be used to pretreat silicon steel slag. The objective of this study was to form

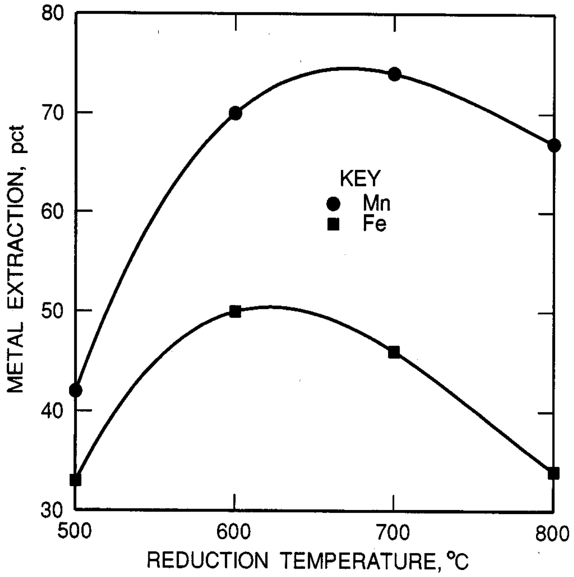

Figure 3.—Extraction of manganese and iron from silicon steel slag as function of reduction temperature.

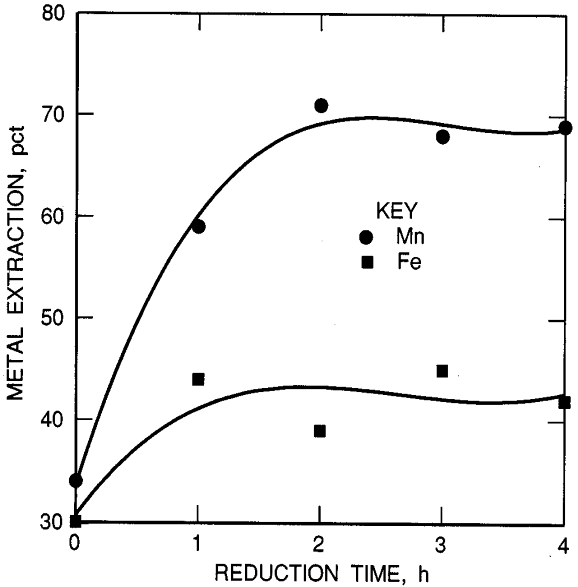

Figure 4.—Extraction of manganese and iron from silicon steel slag as function of hydrogen reduction time at 700° C.

magnetite (Fe_3O_4), which previous research showed to be refractory to ammonium carbamate leaching, and determine whether iron extraction could be inhibited without decreasing manganese extraction. In each test, minus 100-mesh silicon steel slag was treated in various gases, as outlined in table 3, and then leached in carbamate solution. The results of the leaching tests are summarized in table 4. Although magnetite was formed by air oxidation and iron extraction was decreased, manganese solubilization was also depressed. The data in table 4 show that only hydrogen pretreatment improved manganese extraction, compared with the untreated, as-received slag.

Table 3.—X-ray analyses of as-received and pretreated silicon steel slag[1]

Slag pretreatment	*Identified species*
As received	Major FeO, β-Ca_2SiO_4, $CaFeO_2$; minor unidentified.
Heated in air	Major Fe_3O_4, β-Ca_2SiO_4; minor amorphous, $CaFeO_2$; possible $Ca_2MgFe_2O_6$.
Heated in air and then in 20 CO-80 CO_2.	Major Fe_3O_4, β-Ca_2SiO_4; minor amorphous, $Ca_2MgFe_2O_6$, $Ca_2Fe_2O_5$; trace unidentified.
Heated in 20 CO-80 CO_2 ..	Major FeO; minor amorphous, β-Ca_2SiO_4, $CaFeO_2$; possible minor $Ca_2MgFe_2O_6$, $Ca_2Fe_2O_5$; trace unidentified.
Heated in CO	Major FeO; minor $Ca_2Fe_2O_5$, $CaFeO_2$; possible minor β-Ca_2SiO_4, $Ca_6Fe_7O_5$.
Heated in H_2	Minor FeO, amorphous, $Ca_2Fe_2O_5$, $CaFeO_2$, β-Ca_2SiO_4; trace $Ca_2Mg(SiO_4)_4$.

[1] All heat treatments for 2 h at 700° C.

Table 4.—Carbamate leaching of pretreated silicon steel slag[1]

Pretreatment	Leaching time, h	Extraction, pct			
		Mn	Fe	Ca	Mg
As received ..	6	34	30	5.8	0.4
Air	6	1	.5	1.7	.99
Air-CO-CO_2 ..	6	5	6	1.1	.11
CO-CO_2	6	8	6	5.4	.37
CO	6	36	31	5.1	.59
H_2	4	71	50	1.0	.50

[1] Pretreatment conditions: 700° C, 2 h (see table 3). Leaching conditions: 18 g of slag per 100 g of leachant containing a 4.5 mol ratio of NH_3-to-CO_2, ambient temperature.

EFFECT OF LEACHING TIME

To determine the effect of leach time on manganese extraction, 18-g samples of minus 100-mesh slag were reduced with hydrogen at 700° C for 2 h, and the samples were then leached at ambient temperature in a single stage for various time periods using 100 g of leaching solution containing a 4.5 mol ratio of ammonia to carbon dioxide. As shown in figure 5, selective leaching of manganese and

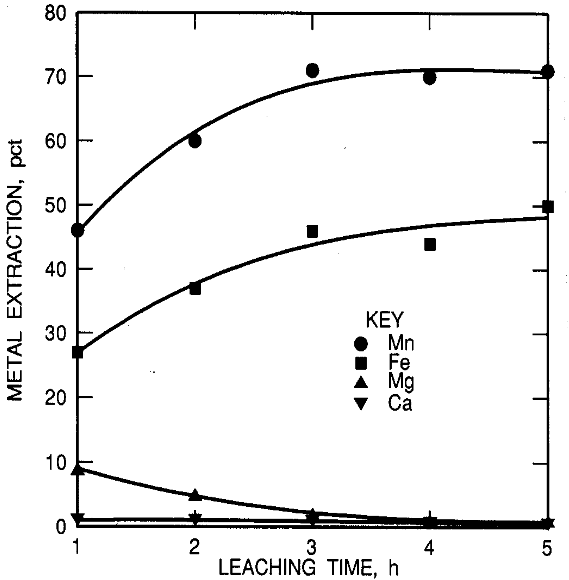

Figure 5.—Extraction of manganese, iron, magnesium, and calcium from 700° C hydrogen-reduced silicon steel slag as function of leaching time.

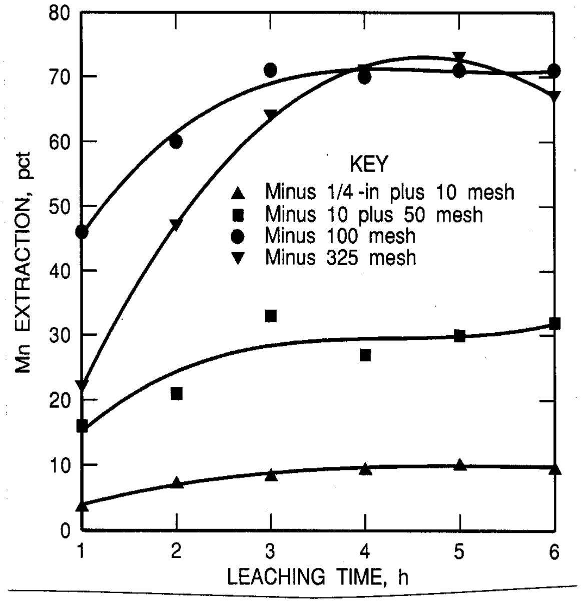

Figure 6.—Effect of grind size on extraction of manganese from silicon steel slag.

iron was achieved after 4 h, with the other principal components of the slag, calcium and magnesium, reporting to the tails. Some calcium and magnesium were initially solubilized, but they were precipitated after longer leaching periods. Manganese and iron extractions after 4 h were 71 and 48 pct, respectively, but less than 1 pct of the calcium and magnesium were coextracted. Very little or no phosphorus was extracted. Phosphorus levels in solution were below the analytical detection limit (30 mg/L).

EVALUATION OF PARTICLE SIZE

The effect of particle size on extraction of manganese from hydrogen-reduced silicon steel slag is summarized in figure 6. As expected, the extent and rate of leaching increased as the slag was ground finer. Decreasing the particle size from minus 1/4 in plus 10 mesh to minus 100 mesh increased the manganese extraction after 6 h from 10 to 71 pct. Decreasing the particle size to minus 325 mesh had little further effect on the manganese extraction.

EFFECT OF PULP DENSITY ON CARBAMATE LEACHING

The amount of slag solids in solution was varied to determine the effect of pulp density on manganese extraction from the slag. In these tests, 10- to 36-g samples of minus 100-mesh prereduced slag were leached for 6 h in 100 g of carbamate solution containing a 4.5 mol ratio of ammonia to carbon dioxide. The leaching rate profiles are shown in figure 7. Best results were obtained at lower pulp densities, between 10 and 18 g of solids per 100 g solution. Increasing the slurry solids to 25 and 36 g per 100 g of solution decreased the maximum manganese extractions from between 67 and 75 pct to between 47 and 60 pct. Most subsequent testing was conducted using 18 g of slag in 100 g of solution.

COMPOSITION OF CARBAMATE LEACH SOLUTION

The weights of concentrated ammonium hydroxide and ammonium carbamate used to make up the leach solutions were varied, as summarized in table 5, to determine the effect of the solution's ammonia-to-carbon dioxide mole ratio on manganese extraction. In each test, minus 100-mesh silicon steel slag was reduced in hydrogen for 2 h and leached for 6 h in 100 g of solution. Mole ratios of 3.2, 4.5, 5.5, and 7.0 were evaluated, and the leaching results are reported in figure 8. In the 3.2 and 5.5 range, the mole ratio appeared to have little effect on manganese solubilization, and maximum extractions were between 70 and 75 pct. But extraction decreased somewhat when the ratio was increased to 7.0. A 4.5 mol ratio was chosen for further tests.

Table 5.—Composition of carbamate leaching solutions, grams

Mole ratio NH_3-to-CO_2	NH_4OH	$NH_2CO_2NH_4$	H_2O
3.2	39	44	17
4.5	54	29	17
5.5	28	71	1
7.0	21	77	2

MULTIPLE-STAGE LEACHING

To determine whether manganese extraction from the silicon steel slag could be increased beyond 71 pct, multiple-stage leaching experiments were conducted. Eighteen-gram samples of minus 100-mesh slag were reduced in hydrogen at 700° C for 2 h and leached in four consecutive 4-h leaching tests, each containing 100 g of fresh carbamate solution. The slurries were filtered between stages. The solids were washed only after the fourth stage.

Figure 9 shows that releaching did increase manganese solubilization to over 80 pct, but little improvement was seen beyond two stages. First-stage extraction was less than normal in this experiment (67 pct), because the solids, which undoubtedly contained some solubilized manganese, were not washed between stages. Between the second and fourth stages, manganese extraction increased by only 3 pct to a total of 83 pct, which is probably due only to filtering and washing of the slag after the final leach.

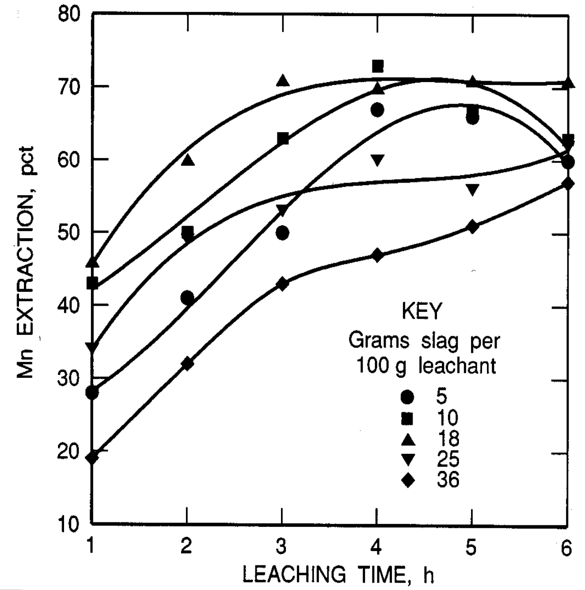

Figure 7.—Effect of pulp density on extraction of manganese from silicon steel slag.

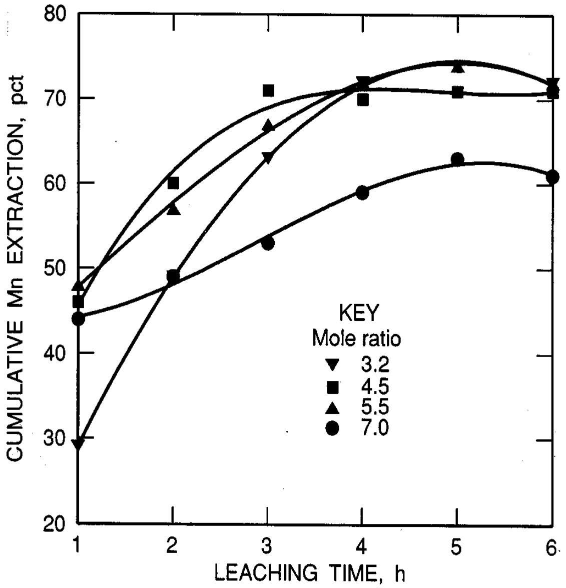

Figure 8.—Effect of ammonia-to-carbon dioxide mole ratio on extraction of manganese from silicon steel slag.

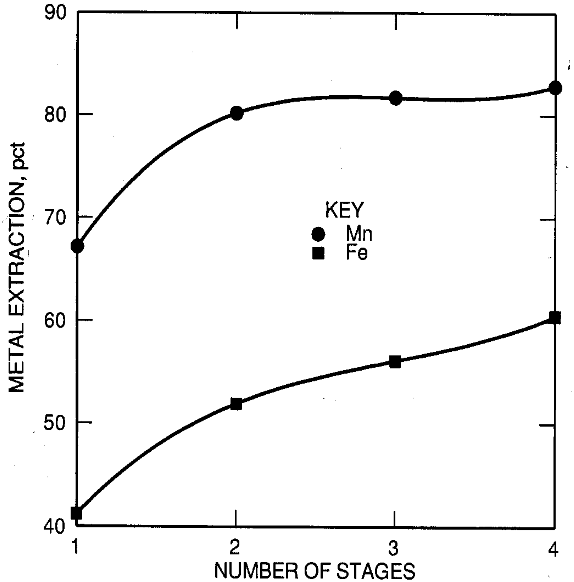

Figure 9.—Multiple-stage leaching of silicon steel slag.

Photomicrographs of leached silicon steel slag showed that carbamate attack occurred at the surface of the particles and rounded the edges. After leaching, the surface of the particles consisted mainly of dicalcium silicate. The manganese remaining in the slag appeared to be entrapped by this refractory silicate and shielded from the leaching solution, resulting in incomplete manganese recovery.

PRECIPITATION OF MANGANESE AND IRON FROM CARBAMATE SOLUTIONS

To complete the process of recovering manganese and iron from the silicon steel slag, the metal values were precipitated from pregnant solution as carbonate salts by evaporative removal of ammonia. As shown in table 6, more than 99 pct of the manganese could be precipitated from solution, but the recovery rate was dependent on temperature. Complete precipitation took 3 h at 65° C, 20 min at 75° C, and at 85° C was complete by the time the solution reached temperature, which took only 10 to 12 min. The solids were easily filtered and a typical precipitate contained, in percent, 8.5 manganese, 39.5 iron, 0.9 magnesium, 0.6 calcium, and less than 0.1 phosphorus. X-ray diffraction analysis identified only manganese and iron carbonate salts. The carbonate precipitate could be used as a source of manganese in the steelmaking industry or purified and sold as a separate product.

Table 6.—Effect of heating time and temperature on precipitation of manganese and iron from pregnant solution

Temperature of heating, °C	Time at temperature, min	Percentage removed	
		Mn	Fe
85	10	99.9	99.9
	5	99.8	99.8
	0	99.9	99.9
75	25	99.9	99.9
	20	99.5	99.4
	15	75.7	76.1
65	240	99.4	83.9
	180	99.2	82.3
	150	86.6	63.5

AMMONIUM CARBAMATE LEACHING OF OTHER STEELMAKING SLAGS

Carbon and silicon-carbon steel slags in table 1 were leached in carbamate solution using the experimental conditions developed using the silicon steel slag. Each slag was crushed to minus 100 mesh and reduced in hydrogen at 700° C for 2 h. Eighteen grams of reduced slag was leached in a single stage for 6 h in 100 g of carbamate solution containing a 4.5 mol ratio of ammonia to carbon dioxide.

Carbamate leaching of these slags was less successful than leaching silicon steel slag. As shown in table 7, manganese extraction was 45 pct from the Indiana Harbor, IN, carbon steel slag; 51 pct from the Warren, OH, carbon steel slag; and only 7 pct from the Natrona Heights, PA, silicon-carbon steel slag, compared with 71 pct from the Warren, OH, silicon steel slag.

Table 7.—Carbamate leaching of other slags, percent extraction[1]

Location and type of steel	Mn	Fe	Mg	Ca
Indiana Harbor, IN: C	45	12	3.1	0.40
Natrona Heights, PA: Si-C ..	7	13	1.4	.60
Warren, OH:				
Si	71	50	1.0	.50
C: Sample 1	51	34	1.4	.16

[1] Pretreated in H_2 at 700° C for 2 h.

The low leachability of the silicon-carbon steel slag may be attributed to the fact that this manganese was associated only with the refractory silicate phase, as discussed earlier.

Differences in the grain size and composition of the slags and the inability of the leachant to permeate the entire particle are factors contributing to the variation in manganese extraction from the other three slags. In particular, the small grain size of the carbon steel slag from Indiana Harbor would be expected to have a marked effect on the extraction of manganese. Indeed, carbamate leaching solubilized only 45 pct of the manganese from this slag, probably because manganese-bearing grains were encapsulated by the silicate phase.

Attempts were made to liberate the components of the slags by fine grinding. Photomicrographs of minus 200- plus 325-mesh and minus 325-mesh fractions showed that breakage occurred across the phase boundaries and even minus 325-mesh size particles contained mixtures of the phases. Costs for grinding to completely liberate particles as small as the 5-μm manganese-bearing grains seen in some of these slag samples would be excessive, particularly since slag grades and manganese values are low.

Several samples were exposed to a 3-kW microwave source to determine whether thermally induced breakage would occur. Minor cracking did occur but, again, not along phase boundaries. The grinding and microwave studies show that except for magnetic separation of steel prills, which is commonly practiced, grinding or other physical beneficiation techniques are not able to separate the slag components and upgrade the manganese values in these slags.

SUMMARY AND CONCLUSIONS

This research has shown that manganese can be recovered from a silicon steel BOF slag by ammonium carbamate leaching. Conditions were optimized to dissolve about 80 pct of the manganese and 50 pct of the iron present in the slag. Phosphorus remained in the tails. Manganese and iron were recovered from the pregnant solutions as a mixture of carbonate salts by heating and removing ammonia.

The optimum conditions developed for recovering manganese from the silicon steel slag did not produce such favorable results when used on carbon and silicon-carbon steel BOF slags. The disparate results can be attributed to variabilities in the phase composition and grain sizes within the particles of the different slags. Photomicrographs indicate that leaching ceased when particle surface layers of refractory dicalcium silicate were exposed. Manganese deep within the slag particles appeared to be untouched by the leachant. Attempts to separate the phases in the slag particles by fine grinding or microwaving were unsuccessful.

Because of (1) the high cost of reductive roasting, (2) the low grade of the slags, and (3) the fact that ammonium carbamate leaches manganese from some steelmaking slags but not others, further development of this process is not recommended at this time. Ammonium carbamate leaching could feasibly be utilized in the future if strategically necessary. Meanwhile, other methods for recovering manganese from domestically produced materials should be sought.

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