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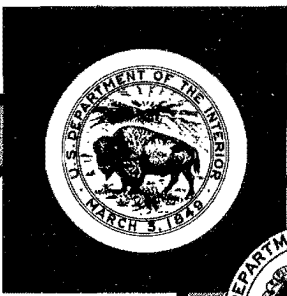
REPORT OF INVESTIGATIONS/1991

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Leaching Basic Oxygen Furnace Slag With Fluosilicic Acid To Recover Manganese and Byproducts

By J. E. Meacham, L. E. Schultze, E. G. Baglin, and J. A. Eisele

UNITED STATES DEPARTMENT OF THE INTERIOR



BUREAU OF MINES

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TO RECOVER MANGANESE AND BYPRODUCTS

By J. E. Meacham, L. E. Schultze, E. G. Baglin, and J. A. Eisele

ERRATA

On page 2, the second sentence of the second paragraph should read as follows:

The principal sources of these imports were the Republic of South Africa, Gabon, France, and Mexico.

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**UNITED STATES DEPARTMENT OF THE INTERIOR
Manuel Lujan, Jr., Secretary**

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T S Ary, Director**

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mg	milligram
g	gram	mg/L	milligram per liter
g/g	gram per gram	mL	milliliter
h	hour	pct	percent
in	inch	ppm	part per million
L	liter	rpm	revolution per minute
lb	pound	st	short ton
lb/st	pound per short ton	wt pct	weight percent
μm	micrometer		

LEACHING BASIC OXYGEN FURNACE SLAG WITH FLUOSILICIC ACID TO RECOVER MANGANESE AND BYPRODUCTS

By J. E. Meacham,¹ L. E. Schultze,² E. G. Baglin,² and J. A. Eisele³

ABSTRACT

The U.S. Bureau of Mines investigated recovery of manganese from basic oxygen furnace (BOF) steelmaking slags because the slags represent a large potential resource of a metal for which there is no domestic production. BOF slags were leached using fluosilicic acid, a byproduct of the fertilizer industry. Manganese and iron were extracted as soluble manganous and ferrous fluosilicates while the calcium and magnesium remained in the tailings as insoluble fluorides. Treating the pregnant liquor with sodium chloride, precipitated sodium fluosilicate (Na_2SiF_6), which was recovered as a byproduct. Manganese and iron were precipitated as hydroxide-carbonate salts with the addition of sodium carbonate to the treated liquor. Recoveries for manganese and iron were 73 to 83 and 67 to 70 pct, respectively.

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INTRODUCTION

Manganese serves two functions in the steelmaking process; it is an alloying agent improving such properties as strength, toughness and hardenability, and it is also used to control sulfur. Manganese controls sulfur by forming manganese sulfide instead of iron sulfide, which would make the steel brittle. The average manganese content for all types of steel is 8.7 lb/st or 0.44 pct. The United States has no high-grade manganese deposits (containing 35 pct or more manganese) and no economical methods of recovering manganese from its low-grade deposits exist. Consequently, there is no domestic production of manganese, and the United States is completely dependent upon foreign sources for manganese.

In 1987, the United States imported 340,000 st of manganese ore, 360,000 st of ferromanganese and 191,000 st of silicomanganese to produce 89.3 million st of steel (1).⁴ The principal sources of high-grade manganese imports are the USSR, Republic of South Africa, Brazil, and Gabon. The United States will continue to be dependent upon world resources unless domestic resources can be utilized. One such domestic manganese resource is BOF steelmaking slags.

The trend in iron and steel production is away from the older, less efficient open-hearth furnaces to the BOF furnace. Currently, about 60 pct of the steel manufactured in the United States is produced in BOF furnaces. By the 1990's, BOF furnaces will account for over 80 pct of the production of steel from iron ore (2).

In the BOF process for making steel, hot metal from the blast furnace is directly charged to a steelmaking furnace where the carbon and silicon content of the melt is adjusted. Fluorspar (CaF_2) is also added to the melt to control viscosity. A slag phase is formed on top of the molten steel by the addition of lime. Impurities are oxidized and report to the slag.

Approximately 40 pct of the slag is recycled to the blast furnace, but the remainder is discarded because of its high phosphorus content (3). Phosphorus is a highly corruptive substance in steel, increasing brittleness and lowering strength and corrosion resistance in concentrations of less than 0.05 pct. Attempts to remove phosphorus from BOF

slags by slow crystallization and physical separation have been only minimally successful (4).

Discarded iron and steel slags are consumed mainly by the construction industry as substitutes for natural aggregates and other construction materials. Slags have been used in place of other materials because of their lower costs, superior performance for many applications, or shortages of natural aggregates (5). However, using slag as aggregate does not utilize the manganese values still present.

Discarded slag represents a loss of manganese value. It is estimated that 3.8 million st of BOF slag containing 133,000 st of manganese are discarded annually. BOF slags range in manganese content from 1 to 7 pct and average 3.5 pct (6). BOF slags are a possible domestic source of manganese the United States could use if economical recovery methods were found.

The U.S. Bureau of Mines examined manganese recovery from steelmaking slags as early as the 1950's. The high silica content of open-hearth slags made them refractory to hydrometallurgical treatment. To liberate the manganese, the slag was clinkered with lime, reduced with hydrogen gas, and leached with ammonium carbamate solution (7). With the switch from the open-hearth furnace to the BOF for producing iron, a different type of slag exists today. BOF slags are composed primarily of lime, with very little silica present. Direct ammonium carbamate leaching of BOF slags, without clinkering, has met with only limited success. Since phosphorus removal from BOF slags and older methods of manganese recovery have met with limited success, a new process for recovering manganese from BOF slags would be advantageous.

This investigation studied hydrometallurgical methods to separate and recover manganese from BOF slags. The recovered manganese is to be used as a substitute for manganese ore fed into the blast furnace. Fluosilicic acid byproduct from the fertilizer industry was used as a leachant. The major advantage of this process is that a byproduct, fluosilicic acid, is used to leach manganese from another byproduct, BOF slags. The primary concern was to maximize manganese recovery by optimizing such parameters as: agitation rate, temperature, fluosilicic acid content, pulp density, particle size, and number of leaching stages.

⁴Italic numbers in parentheses refer to items in the list of references at the end of this report.

EXPERIMENTAL

MATERIALS

The slag samples tested were from four different BOF furnaces: high silicon (Ohio), silicon (Ohio), carbon (Ohio), and silicon (Pennsylvania). Each slag sample was ground to pass 100 mesh. The chemical compositions of the slag samples are presented in table 1. Different size fractions of minus 14 plus 28, minus 28 plus 48, minus 48 plus 100, minus 100 plus 200, minus 200 plus 400, and minus 400 of the silicon steel slag sample (Ohio) were prepared to study the effect of particle size in the extraction of manganese.

The slag samples were leached using fluosilicic acid (H_2SiF_6), a byproduct of the fertilizer industry. Fluosilicic acid is recovered when stack gases are scrubbed during the processing of phosphate fertilizers. A chemical profile of the acid byproduct used is presented in table 2. All other chemicals used were reagent grade.

PROCEDURE AND EQUIPMENT

Leaching was carried out in a 500-mL resin kettle glass reactor fitted with a reflux condenser and a thermocouple. The reactor was heated with a mantle controlled by an energy regulator and agitated by a 3- by 3/4-in Teflon fluorocarbon polymer anchor glass shaft stirring assembly. Agitation speed was controlled by a voltage regulator.

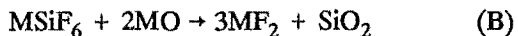
EXPERIMENTAL RESULTS AND DISCUSSION

SINGLE STAGE LEACHING

When slag is mixed with fluosilicic acid, calcium, iron magnesium and manganese are all extracted as fluosilicates;



where M = Mn, Fe, Ca, and Mg. Selective extraction of manganese and iron is pH dependent. As fluosilicic acid is neutralized by lime contained in the slag, the pH of the solution rises and calcium and magnesium fluorides are precipitated:



where M = Ca and Mg. At a pH of 4.5, most of the calcium and magnesium have been precipitated. Manganese

and iron remain in solution as soluble fluosilicate salts at pH 4.5.

To find the conditions that would yield maximum manganese extraction, tests were conducted in which agitation rate, temperature, acid content, mesh size, pulp density, and leaching time were varied. To assure that evaluation of variables was not influenced by slag composition, all single stage leaching tests were done using the silicon (Ohio) steel slag sample.

Table 1.—Composition of steelmaking slag samples, weight percent

Type of steel production	Mn	Fe	CaO	MgO	P ₂ O ₅	SiO ₂
High silicon (OH) . . .	1.1	3.0	38	9.6	0.48	37
Silicon (OH)	3.0	26	36	9.6	.64	10
Carbon (OH)	3.3	21	39	7.3	.46	13
Silicon (PA)	3.1	19	36	11.3	.76	19

Table 2.—Composition of fluosilicic acid byproduct, grams per liter

H ₂ SiF ₆	301
Cl	1.7
SO ₄64
P34
Ca05
Fe04

Effect of Agitation Rate

The effect of agitation rate on manganese extraction was studied using slag samples of minus 100 mesh size. A pulp density of 9.9 pct, an acid content of 0.94 g of H_2SiF_6 per gram of slag, a temperature of 95° C, and a leaching period of 5 h were used. Under these conditions, 69.3 pct of the manganese was extracted at an agitation

rate of 160 rpm. Increases of the agitation rate to 320 and 640 rpm gave no increase in extraction. In subsequent experiments, an agitation rate of 320 rpm was used, and the above conditions were maintained while only one parameter at a time was varied.

Effect of Temperature

The effect of temperature over the range 50° to 95° C was investigated, and manganese extraction was plotted as a function of time (fig. 1). Manganese extraction rate increased as the temperature increased from 50° to 95° C, but total of extraction did not. At 50° C, extraction reached a maximum of 69 pct after 5 h at a final pH of 4.4, while at 95° C, this maximum and final pH were reached after only 3.5 h of leaching.

Temperature had a profound effect on calcium and magnesium concentration in the pregnant liquor. Initially, the pH of the slurry is low and calcium and magnesium are soluble. With time, fluosilicic acid is neutralized by lime contained in the BOF slags, and the pH of the leach solution increases, precipitating calcium and magnesium as insoluble fluorides. With an increase in temperature, the reaction rate of this neutralization is increased and calcium and magnesium are precipitated more rapidly and more completely. Since at higher temperatures both manganese extraction and calcium and magnesium precipitation rates were increased, 95° C was selected as the standard leaching temperature.

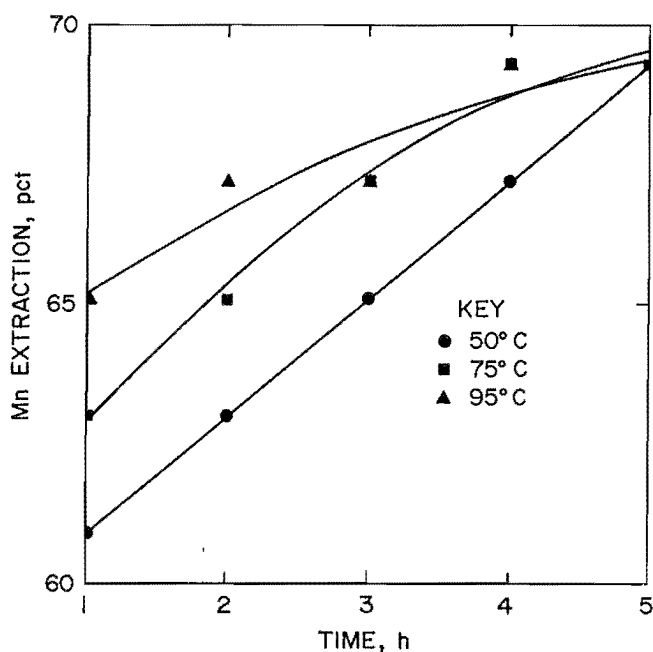


Figure 1.—Manganese extraction as function of time for temperatures of 50°, 75°, and 95° C.

Fluosilicic Acid Requirements

The acid requirements for leaching manganese from silicon steel slag were evaluated. Leaching tests were performed using 0.75 to 1.32 g of H_2SiF_6 per gram of slag (66 to 117 pct of stoichiometric as defined by reactions A and B). From figure 2, increasing the acid content above 0.94 g of H_2SiF_6 per gram of slag (83 pct of stoichiometric) did not increase total manganese extraction. However, at higher acid content, the extraction rate increased.

Higher acid content resulted in higher concentrations of calcium and magnesium in the final pregnant liquor. As acid is consumed and the pH increases, calcium and magnesium fluorides are precipitated. In the tests that used 1.13 and 1.32 g of H_2SiF_6 per gram of slag (100 and 117 pct of stoichiometric), excess acid existed in the final pregnant liquor. Consequently, the pH of the final pregnant liquors was too low (2.2 and 1.8, respectively) to precipitate all of the calcium and magnesium. Since maximum manganese extraction and minimum calcium and magnesium concentration are desired, an acid content of 0.94 g of H_2SiF_6 per gram of slag was selected as a standard.

Effect of Pulp Density

Leaching tests were performed to determine the effect of pulp density on manganese extraction. Pulp densities of 8.8 to 13.2 pct were evaluated. At pulp densities of

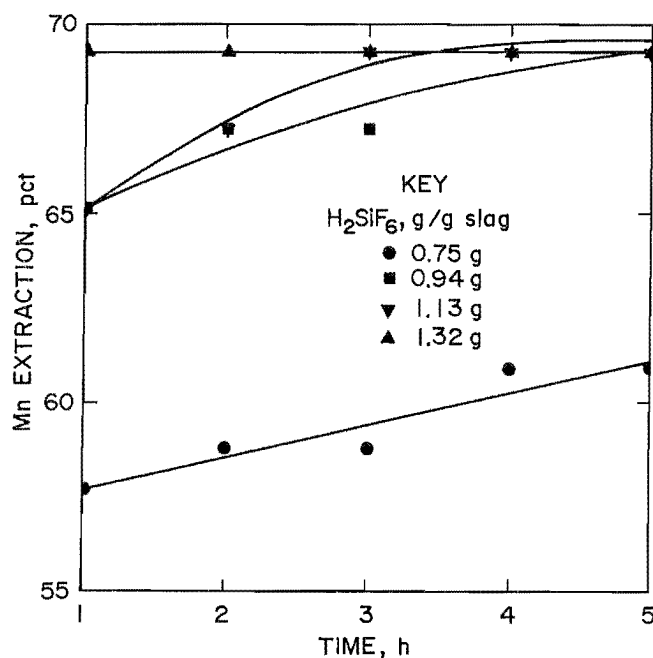


Figure 2.—Manganese extraction as function of time with increasing quantity of fluosilicic acid.

13.2 and 11.3 pct, manganese was precipitated from solution during the leach (fig. 3). This phenomenon did not occur using pulp densities of 9.9 and 8.8 pct. The higher the pulp density, the more quickly calcium and magnesium were precipitated as fluorides. Since maximum manganese extraction and minimum calcium and magnesium solution concentrations are desired, a pulp density of 9.9 pct was chosen.

Effect of Particle Size

The effect of particle size was studied using minus 14 plus 28, minus 28 plus 48, minus 48 plus 100, minus 100 plus 200, minus 200 plus 400, and minus 400 mesh fractions. Leaching time was increased to 6.0 h to compensate for the slower dissolution of the larger mesh sizes. Results are shown in figure 4. There was a 9.2 pct increase in manganese extraction when comparing the minus 28 plus 48 to the minus 48 plus 100 mesh fractions. When silicon steel slag was ground finer than minus 48 plus 100 mesh, manganese extraction rate increased, but manganese extraction was not improved.

Fluosilicic acid was consumed more quickly when finer mesh material was used, due to the greater surface area of the finer material. This increase in the acid consumption rate caused calcium and magnesium to precipitate more rapidly. All further work was done on minus 100 mesh material.

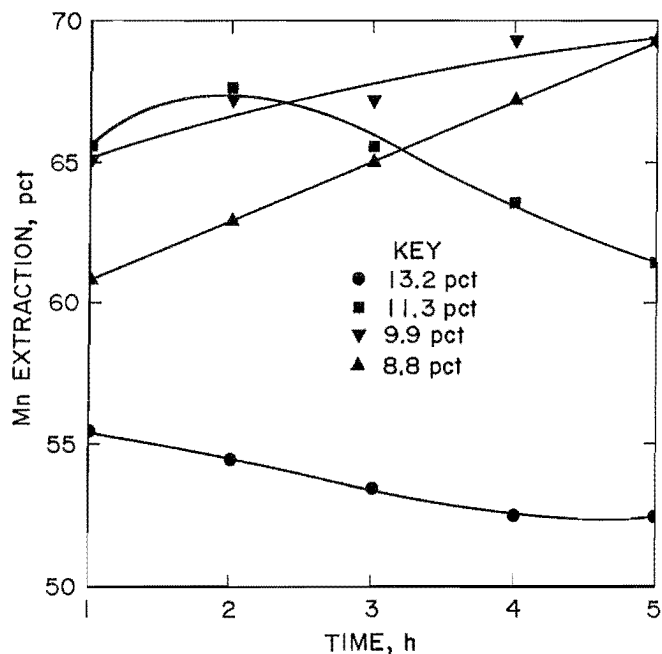


Figure 3.—Manganese extraction as function of time with decreasing pulp density.

TWO-STAGE COUNTERCURRENT LEACHING

During single stage leaching, two distinct leaching steps were identified; solubilization of calcium, iron, magnesium, and manganese followed by precipitation of calcium and magnesium. To increase extraction of manganese and rejection of calcium and magnesium, a two-stage countercurrent leach was investigated.

Silicon (Ohio) steel slag was leached countercurrently as shown in figure 5. Forty grams of slag ground to minus 100 mesh was placed in reactor 2 and mixed with pregnant liquor exiting reactor 1. It was leached at a pulp density of 10.7 pct, a temperature of 95° C, for a duration of 2.0 h. After liquid-solid separation, the partially leached slag was transported to reactor 1 where it was mixed with 325 mL of fresh fluosilicic acid containing 37.6 g (equivalent to 0.94 g of H_2SiF_6 per gram of slag) at a pulp density of 9.9 pct and leached at a temperature of 95° C, for a duration of 2.5 h. After filtration, the tailings were washed with 200 mL of deionized water. The wash water was recycled and used to dilute the fluosilicic acid to the desired concentration.

Calcium, magnesium, manganese, and iron were extracted from the slag in reactor 1 (fig. 6). Examining figure 6, manganese and iron extractions reached maximums of 75 and 70 pct, respectively, after 2.0 h of leaching. Precipitation of calcium and magnesium as fluorides

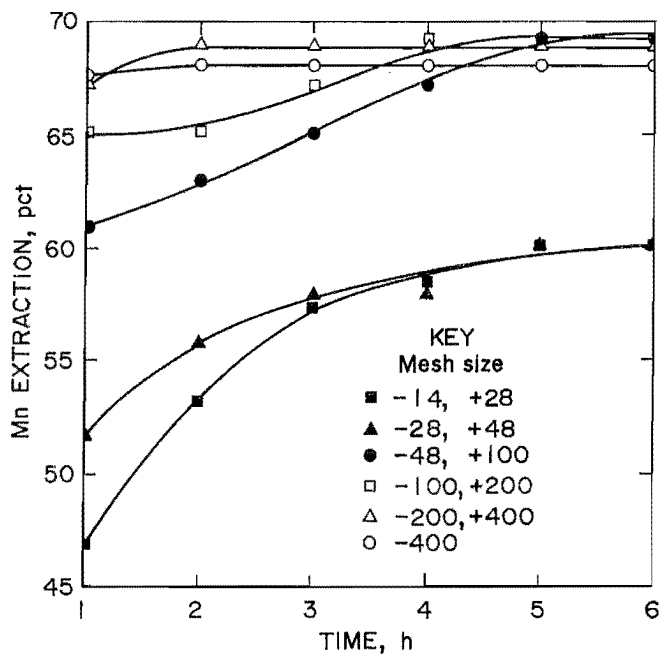


Figure 4.—Manganese extraction as function of time for size fractions.

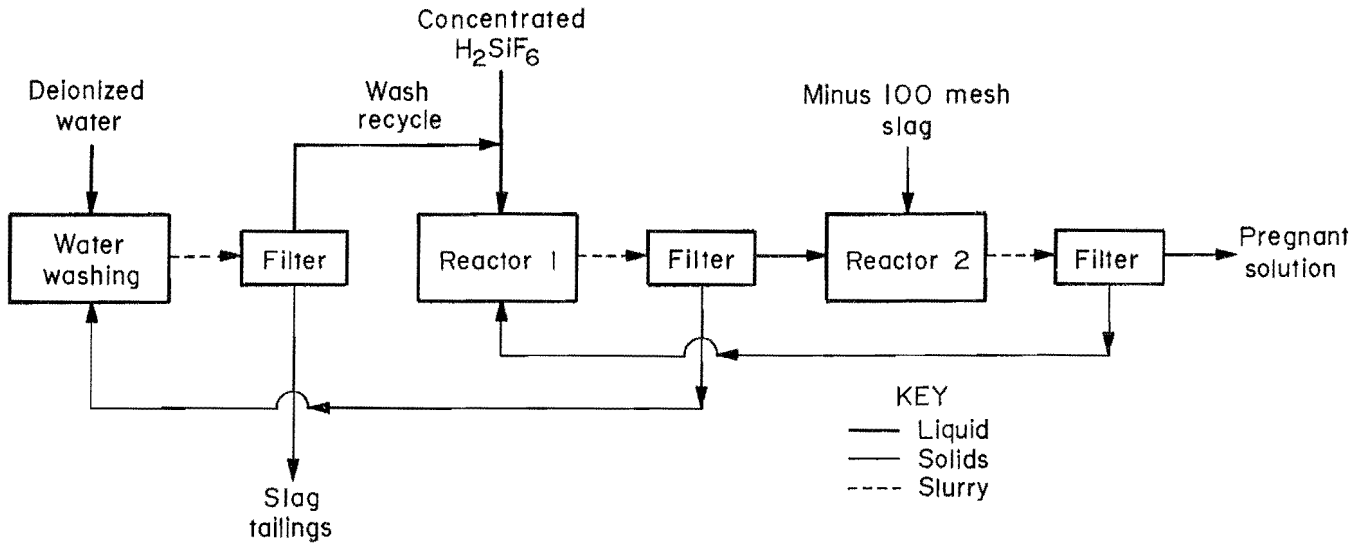


Figure 5. - Two-stage countercurrent leaching of steelmaking slag.

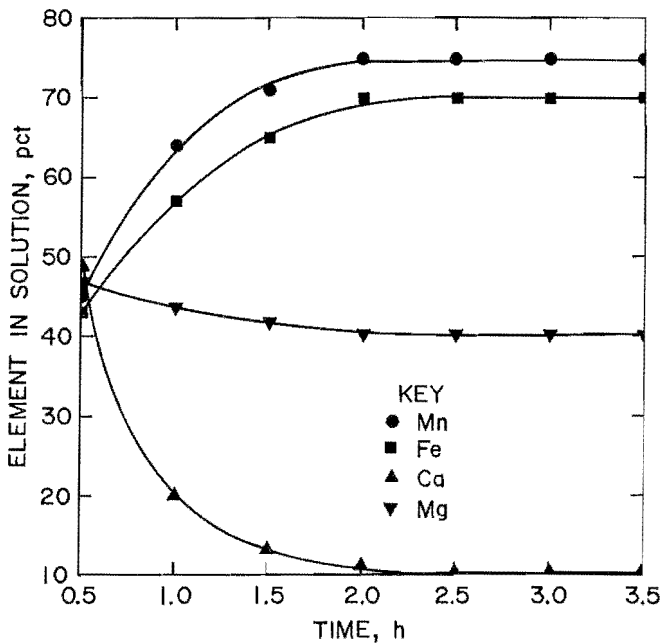


Figure 6.—Extraction as function of time for manganese, iron, calcium, and magnesium in reactor 1.

from the pregnant liquor reached a maximum after 2.5 h. At a final pH of 1.9, 10 pct of the calcium and 40 pct of the magnesium remained in the pregnant liquor. To assure reactions in reactor 1 are completed, a leaching time of 2.5 h is recommended.

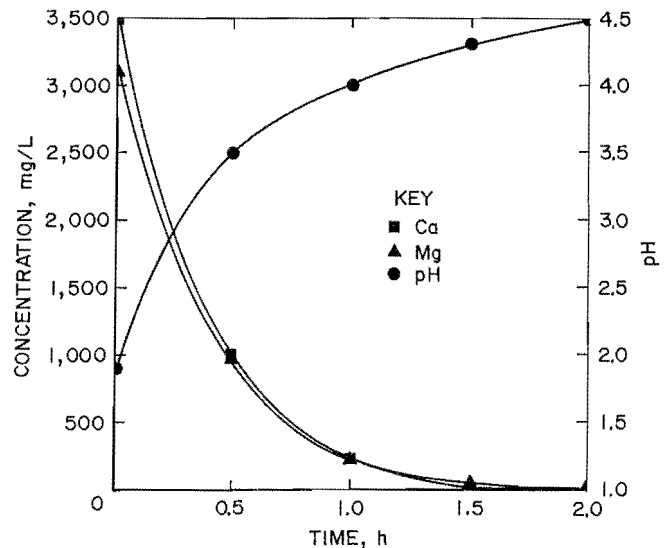


Figure 7.—Calcium and magnesium concentration and pH value as function of time in reactor 2.

In reactor 2, the pregnant liquor was mixed with sufficient slag containing residual lime to raise the pH to 4.5 (fig. 7). At pH 4.5, manganese and iron remained in solution as soluble fluosilicates, while the remaining calcium and magnesium were precipitated as insoluble fluorides. Calcium concentration in the pregnant liquor decreased until a minimum of 8 mg/L was reached after

2.0 h. Magnesium concentration reached a minimum of 16 mg/L after 2.0 h. Iron and manganese remained soluble in reactor 2, and their concentrations remained constant.

Best manganese and iron extractions for the single stage leach were 69 and 63 pct, respectively. The minimum calcium and magnesium concentrations obtained during the single stage leach were 290 and 460 mg/L, respectively. When a two-stage countercurrent leach was performed, manganese and iron extraction improved to 75 and 70 pct, while calcium and magnesium concentrations in the final pregnant liquor were decreased to 8 and 16 mg/L, respectively. Two-stage countercurrent leaching increased manganese and iron extraction and improved selectivity with respect to calcium and magnesium. Therefore, a two-stage countercurrent leach is recommended. Photomicrograph and X-ray diffraction analysis of the slag tailings did not reveal why 75 pct Mn extraction could not be exceeded.

To determine if two-stage countercurrent leaching would work on other BOF slags, tests were performed on the three other BOF slag samples available. Table 3 shows that the leaching technique was effective on all the BOF steelmaking slags tested.

Table 3.—Total extraction of manganese and iron from steelmaking slags using two-stage countercurrent leaching, percent extraction

Type of steel production	Mn	Fe	Ca	Mg
High silicon (OH)	75	68	<0.1	0.13
Silicon (OH)	75	70	<.1	.13
Carbon (OH)	83	67	<.1	.10
Silicon (PA)	73	68	<.1	.17

RECOVERY OF MANGANESE FROM SOLUTION

Having demonstrated a satisfactory method for leaching BOF slags, efforts were directed toward methods for recovering manganese and iron from the pregnant liquor. Methods for precipitating manganese from leach liquors were investigated. Best results were obtained using sodium chloride and sodium carbonate and are discussed in the following section.

Recovery of Manganese Using Sodium Hydroxide

A simple method to recover manganese from the pregnant liquor would be the addition of a reagent, which would precipitate the manganese. Under basic conditions, Mn^{2+} forms an insoluble hydroxide $Mn(OH)_2$. Precipitation tests were performed on pregnant liquor using sodium hydroxide.

Although sodium hydroxide was successful in precipitating manganese and iron from the pregnant liquor, a problem occurred. Sodium combined with fluosilicate forming an unwanted precipitate, sodium fluosilicate. Using sodium carbonate to precipitate manganese and iron from the pregnant liquor, also resulted in coprecipitation of sodium fluosilicate. Sodium hydroxide and sodium carbonate treatments were unsatisfactory since the manganese-iron product contained sodium fluosilicate, which cannot be recycled to the steelmaking blast furnace.

By adding a solution of sodium chloride to the pregnant liquor, sodium fluosilicate was selectively precipitated while manganese and iron remained in solution as soluble chlorides. The sodium fluosilicate was filtered from the pregnant liquor, and manganese and iron were precipitated as hydroxide-carbonate salts using sodium carbonate.

Recovery of Manganese Using Sodium Chloride and Sodium Carbonate

Since sodium fluosilicate is used in the water treatment industry for water fluoridation, the step to recover it might be a practical addition. To determine the minimum amount of sodium chloride required to precipitate sodium fluosilicate from the pregnant liquor, experiments were conducted using 1.0 to 1.5 times the stoichiometric requirement (fig. 8).

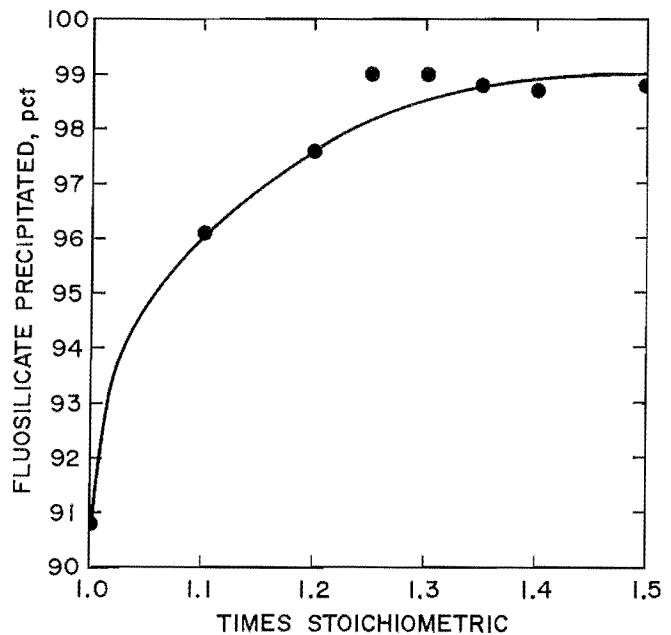


Figure 8.—Fluosilicate precipitated as function of sodium chloride added.

As shown in figure 8, 91 pct of the fluosilicate was precipitated when the stoichiometric amount of sodium chloride was used. A 25-pct excess was required to precipitate 99 pct of the fluosilicate. Addition of more sodium chloride did not precipitate more sodium fluosilicate.

To determine whether the precipitated sodium fluosilicate represented a viable byproduct, information was obtained from the American Water Works Association (AWWA) defining the criteria necessary for use in water fluoridation. There are five specifications that sodium fluosilicate must meet (8). The specifications are as follows:

1. Chemical composition must be 98 pct Na_2SiF_6 by weight.
2. Moisture content must not exceed 0.5 pct by weight.
3. Insoluble matter shall not exceed 0.5 pct by weight.
4. The particle size shall be such that at least 98 pct will pass a U.S. standard sieve No. 40 ($420 \mu\text{m}$) and less than 25 pct shall pass through a U.S. standard sieve No. 325 ($44 \mu\text{m}$).
5. Heavy metals, expressed as lead, shall not exceed 500 ppm by weight.

Analysis of the sodium fluosilicate revealed a concentration of 770 ppm iron, which exceeds the maximum allowable tolerance for metals. To remove impurities, the sodium fluosilicate was washed with $0.5M$ HCl. Specifications 1, 2, 3, and 5 were achieved by the acid washed sodium fluosilicate. Size specification 4 was met after the sodium fluosilicate was agglomerated with 4 pct water and dried for 2 h at 95°C .

With fluosilicate removed, iron and manganese can be precipitated from the pregnant liquor using sodium carbonate. To determine the minimum amount of sodium carbonate required to precipitate manganese and iron, experiments were conducted using 1.0 to 1.5 times the stoichiometric requirement to precipitate manganese and iron as carbonates (fig. 9). At the stoichiometric amount of sodium carbonate, 95 pct of the manganese and iron were recovered as hydroxide-carbonate salts. A 20-pct excess of sodium carbonate was required to precipitate 99 pct of the manganese and iron.

PROPOSED LEACHING-RECOVERY PROCEDURE

Integrating the countercurrent leach scheme with sodium chloride treatment and manganese and iron precipitation, results in the flowsheet shown in figure 10.

Manganese and iron are selectively leached from BOF slag by countercurrent leaching using fluosilicic acid (reactors 1 and 2). Manganous and ferrous fluosilicates

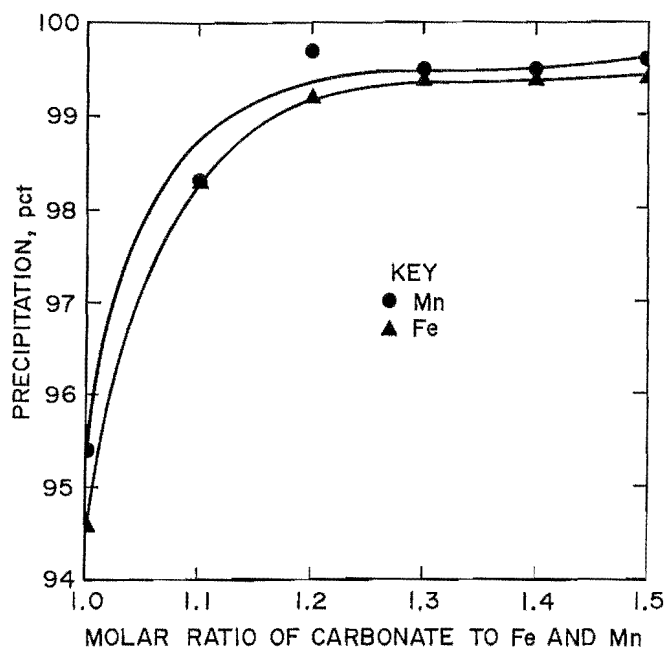


Figure 9.—Percent of manganese and iron precipitated versus molar ratio of carbonate to total manganese and iron.

contained in the pregnant liquor are converted into soluble chloride salts by adding a solution of sodium chloride (reactor 3). Sodium fluosilicate is precipitated and washed with $0.5M$ HCl. The acidic wash water is combined with the recycle stream from sodium carbonate precipitation. Manganese and iron are precipitated from the pregnant liquor by adding a solution of sodium carbonate (reactor 4). The barren solution exiting reactor 4 contains sodium chloride as well as residual sodium carbonate. When the barren stream and wash water from sodium fluosilicate washing are combined, excess sodium carbonate is converted to sodium chloride. The result is a sodium chloride stream with a pH of 6. This stream is concentrated by evaporation and recycled to reactor 3. By recycling the sodium chloride barren stream exiting reactor 4, only a small makeup amount of sodium chloride will be required. A material balance for the process is presented in table 4.

Most process streams in the integrated flowsheet are recycled. Only four streams (table 5) exit in the process; streams 3 (tailings), 23 (sodium fluosilicate), 27 (manganese and iron hydroxy carbonates), and 31 (excess water). Stream 23 is a sodium fluosilicate byproduct, which meets AWWA criteria for water fluoridation. Stream 27 contains manganese and iron, which can be recycled to the steel-making blast furnace after the product is pelletized and

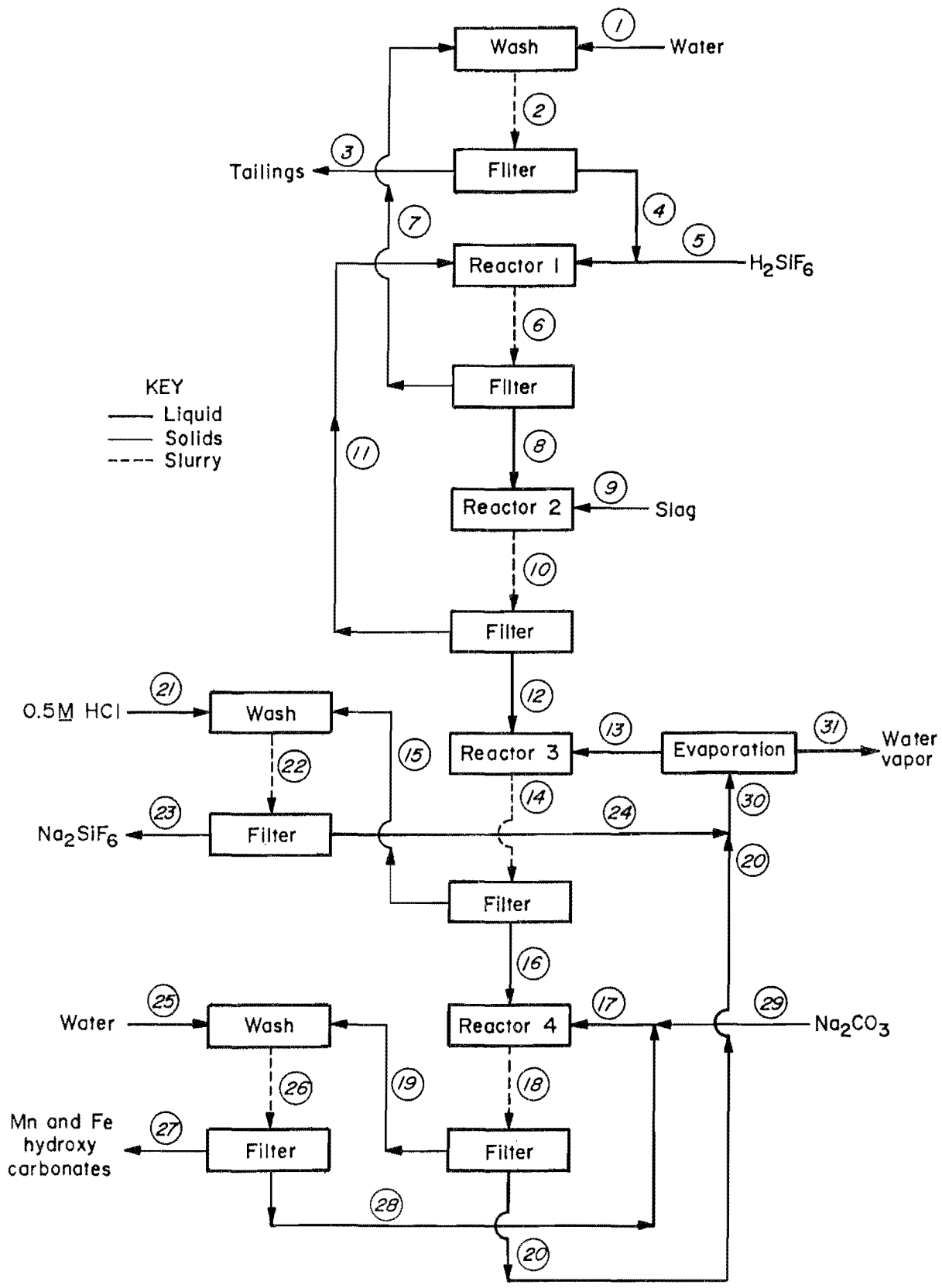


Figure 10.—Process flow diagram.

Table 4.—Mass balances for process

Stream	Temp, °C	Vol, mL	Weight, g	pH	Balances, mg								
					Mn	Fe	Ca	Mg	P	Si	Na	F	
1	A	200	NAp	7.0	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
2	A	NAp	NAp	2.3	700	5,840	10,700	2,510	155	8,160	<.01	23,300	
3	A	NAp	57.3	NAp	300	3,120	10,400	2,320	155	5,310	<.01	13,800	
4	A	200	NAp	2.3	400	2,720	240	190	<.01	2,850	<.01	9,500	
5	A	125	NAp	<0	<.01	5	6	<.01	43	7,330	<.01	29,800	
6	95	NAp	NAp	1.9	2,160	16,000	11,600	3,170	155	15,350	<.01	52,400	
7	A	NAp	NAp	NAp	700	5,840	10,700	2,510	112	8,160	<.01	23,300	
8	95	295	NAp	1.9	1,460	10,200	900	660	<.01	7,190	<.01	29,100	
9	A	NAp	40.0	NAp	1,200	10,400	10,400	2,320	112	1,920	<.01	<.01	
10	95	NAp	NAp	4.5	2,660	20,600	11,300	2,980	112	9,110	<.01	29,100	
11	95	NAp	NAp	NAp	1,760	13,300	11,300	2,980	112	5,170	<.01	13,100	
12	95	190	NAp	4.5	900	7,280	1.5	3	<.01	3,940	<.01	16,000	
13	A	75	NAp	NAp	56	201	<.01	<.01	<.01	31	10,300	289	
14	A	NAp	NAp	4.5	956	7,480	1.5	3	<.01	3,980	10,300	16,300	
15	A	NAp	NAp	NAp	56	200	<.01	<.01	<.01	3,950	6,840	16,200	
16	A	250	NAp	4.5	900	7,280	1.5	3	<.01	25	3,460	93	
17	A	100	NAp	11	1	9	<.01	<.01	<.01	10	8,740	23	
18	A	NAp	NAp	12	901	7,290	1.5	3	<.01	35	12,200	116	
19	A	NAp	NAp	NAp	901	7,290	1.5	3	<.01	14	2,420	27	
20	A	325	NAp	12	<.01	1	<.01	<.01	<.01	21	9,780	89	
21	A	75	NAp	.5	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	
22	A	NAp	NAp	.5	56	200	<.01	<.01	<.01	3,950	6,840	16,200	
23	A	NAp	26.3	NAp	<.01	<.01	<.01	<.01	<.01	3,940	6,320	16,000	
24	A	75	NAp	.5	56	200	<.01	<.01	<.01	10	520	200	
25	A	100	NAp	7.0	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	
26	A	NAp	NAp	11	901	7,290	1.5	3	<.01	14	2,420	27	
27	A	NAp	21.7	NAp	900	7,280	1.5	3	<.01	4	120	4	
28	A	100	NAp	11	1	9	<.01	<.01	<.01	10	2,300	23	
29	A	NAp	22.1	NAp	<.01	<.01	<.01	<.01	<.01	<.01	6,440	<.01	
30	A	400	NAp	6.0	56	201	<.01	<.01	<.01	31	10,300	289	
31	A	325	NAp	6.0	<.01	<.01	<.01	<.01	<.01	<.01	<.01	<.01	

A Ambient temperature. NAp Not applicable.

blended with iron ore. Stream 31 is water vapor from the evaporator, which can be condensed and used as a water source for the process. Only stream 3, the slag tailings, is a waste stream.

Table 5.—Composition of exit streams, weight percent

Stream	Mn	Fe	Ca	Mg	Na	P	Si	F
3 . . . wt pct . .	0.55	6	18	4	¹ <1	0.20	14	180
23 ppm . .	<1	<1	<1	<1	² 24	<1	² 15	² 61
27 ppm . .	² 4	² 32	69	140	² 0.55	<1	180	180

¹Part per million.

²Weight percent.

NOTE: In stream 31, all of these elements were <1 ppm.

Analysis of the slag tailings revealed that they contained 35 wt pct CaF₂ and 28 wt pct SiO₂. Calcium fluoride (fluorspar) has a market value if appropriate specifications can be met.

TREATMENT OF TAILINGS

Flotation

Acid grade fluorspar contains over 97 pct CaF₂, while ceramic grade and steel industry require 90 pct and 60 to

85 pct CaF₂, respectively. An attempt to concentrate the calcium fluoride by flotation was made using oleic acid dissolved in ethanol as a frother. Flotation of the slag tailings yielded disappointing results. Concentrate and tails were almost identical in chemical makeup, indicating separation did not occur.

A scanning electron microscope (SEM) analysis of the slag tailings, flotation concentrate, and flotation tailings revealed why separation did not occur. Calcium fluoride crystals measured 0.1 to 1.5 μm in size and were interlocked with silica. Rather than discrete particles of homogeneous composition, each particle was a clump of different phases. Calcium fluoride appeared to be precipitated on siliceous material as if silica had acted as seed.

Seeding

An attempt was made to increase the size of the calcium fluoride particles by adding fluorspar as seed during the leach. Fluorspar was ground to minus 400 mesh and added to a sample of minus 100 mesh slag. The sample was leached countercurrently as described previously. SEM analysis of the seeded tailings revealed no difference between the unseeded and seeded tailings.

CONCLUSIONS

Methods were investigated to recover manganese from BOF steelmaking slags. Manganese and iron in the slags were leached using fluosilicic acid, which is a byproduct of the fertilizer industry. Manganese and iron formed soluble manganous and ferrous fluosilicate, while calcium and magnesium formed insoluble fluorides. Best extraction and selectivity were achieved using a two-stage countercurrent leach. Sodium fluosilicate was precipitated from the pregnant liquor and recovered as a byproduct using sodium chloride. Manganese and iron were precipitated as hydroxide-carbonate salts with the addition of sodium

carbonate to the treated liquor. Total recoveries for manganese and iron were 73 to 83 and 67 to 70 pct, respectively.

The major advantage of this process is that a byproduct, fluosilicic acid, is combined with slag, another byproduct to form two potential products, manganese and iron hydroxide-carbonate salts, and sodium fluosilicate. Process waste streams are minimized resulting in only one waste stream, the slag tailings. If calcium fluoride could be recovered from the tailings, the tailings would also be a byproduct; however, no satisfactory technique was found.

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