

BENEFICIATION OF UNITED STATES

MANGANESE RESERVES

Economics Research Project  
Princeton University  
15 January 1957

Research Memorandum No. 1

This study was prepared under contract with the Office  
Of Naval Research, and reproduction in whole or in  
part will be permitted for any purpose of the  
United States Government

Technical Report Issued under Office of Naval Research  
Contract No. Nonr-1858(02)

## PREFACE

This study is the first technical report of the investigation of the United States' Manganese problem conducted by the Princeton Economics Research Project. It will soon be followed by further reports describing the overall problem and giving the first mathematical model which applies to it.

This report is largely the work of Mr. Franklin R. Shupp except for Section V which gives a preliminary indication of investigations being carried out by Mr. Herman F. Karreman.

Oskar Morgenstern  
Project Leader

Princeton University  
15 January 1957

## TABLE OF CONTENTS

Section	Page
I INTRODUCTION	1
II DOMESTIC MANGANESE ORE AND SLAG RESERVES	
A. <u>Oxide and Carbonate Ores</u>	
1. Cuyuna Range	3
2. Chamberlain Region	3
3. Artillery Peak	4
B. <u>Silicate Ores and Slags</u>	
1. Aroostook County	5
2. Open Hearth Slags	5
III MANGANESE ORE BENEFICIATION PROCESSES	
A. <u>Oxide and Carbonate Ores</u>	
1. Chemical Processes	
a. Ammonium Carbamate-Carbonate Leach	8
b. Sulfuric Acid and Related Compounds Leach	12
c. Nitric Acid Leach (Nossen)	16
d. Hydrochloric Acid Leach (King)	18
e. Electrolysis	19
2. Physical Processes	
a. Flotation	21
b. Heavy Media Separation and Tabling	22
c. Crushing and Jigging	23
B. <u>Silicate Ores and Slags</u>	
1. Pyrochemical Processes	
a. Lime Clinkering (Sylvester)	24
b. Lime Clinkering-Carbamate Leach (Sylvester-Dean)	25
c. Chlorine Vaporization	27
d. Chemical Roasting (Bruce Williams)	29
2. Pyrometallurgical Processes	
a. Selective Oxidation of Slag-Spiegel (Bureau of Mines)	30
b. Electric Furnace Reduction (Udy)	35
c. Selective Oxidation of Pig Iron (Wright)	36
3. Physical Processes	
High Intensity Arc	38

Section		Page
IV	ALLOY PRODUCTION METHODS	
	A. <u>Ferromanganese</u>	
	1. Blast Furnace	40
	2. Electric Furnace	42
	B. <u>Silicomanganese</u>	43
V	CHARACTERIZATION OF PHYSICAL INPUT COEFFICIENTS AND DOLLAR COST DATA	45

## SECTION I

### INTRODUCTION

This report on domestic ore and slag reserves, and on the proposed beneficiation processes, summarizes the information at present available to the Princeton Economics Research Project. The purpose of the collection is to gather all the technical data needed to construct production functions and to formalize other relationships so that a realistic model for decision making regarding the United States manganese problem can be set up.

The technology in this area is in a state of considerable flux. Thus, there exist processes not listed here; they are omitted because they are too sketchy at present to be included on the technological horizon and no data regarding them could conceivably be obtained by the time we require input data for the intended models. This means that we shall be arguing in the future from the basis of a certain state of the technology, well aware that at a later date some of the processes included here may no longer be of interest while new ones may have appeared. As it is, our task will be to consider all existing processes together, but, of course, they must be in "existence" in a rather definite way. In other words, engineering experience, preferably gained from pilot plant operation, should determine the physical input-output coefficients and the dollar cost relationships. It will be seen from Table 2 in Section V that even for the processes here included the situation is far from satisfactory. In the absence of firm information, we shall have to resort to estimation and this will involve

us in difficult statistical decisions.

The difficulties in obtaining the data presented in this report have been considerable, but we believe that as a result of our efforts most relevant information about beneficiation processes of domestic manganese ore are now available in a convenient form. We wish to thank the many offices and individuals who have so generously assisted us in our attempts. The report may not be entirely free from errors or omissions. It is hoped that these will be speedily brought to our attention; comments will be gratefully received.

In view of the fact that some of the information placed at our disposal must at present be considered as privileged not all the data in our possession are exhibited. We expect to make use of that part of our data only after their express release or in the form of index numbers (whenever feasible) in a manner which will preclude the identification or computation of the restricted figures themselves.

In an attempt to give some order to the apparently unrelated beneficiation processes they will be divided into two categories — those applicable to oxide and carbonate ores, and those best suited to silicate ores and slags. They will be further subdivided according to the nature of their technology, i.e., chemical, physical, pyro-chemical and pyro-metallurgical processes.

## SECTION II

### DOMESTIC MANGANESE ORE AND SLAG RESERVES

Before discussing the various beneficiation processes per se, a brief description of the domestic ore deposits and slag dumps will be outlined. This is quite essential since most of the processes are specific for certain types of ores. Also, both the geological information and the geographical location are key factors in any evaluation of a proposed process. The former is a formidable element in mining costs and the latter is the major determinant of transportation expenditures.

#### A: Oxide and Carbonate Ores

##### 1. Cuyuna Range (Minnesota)

The ore in this deposit is usually considered as the United States' best large reserve. These ores, a mixture of oxides and carbonates, include 50,000,000 tons with an average between 8-10 per cent metal content. In addition, there are probably 500,000,000 tons of ore assaying between 2.5-6 per cent and averaging close to 5 per cent. This ore contains considerable iron and could be strip mined in the same manner as the large iron ore deposits in the region. Costs have been estimated at \$3.00-\$5.00. All estimates include a profit for the mining firms.

The Great Lakes and the iron ore industry provide an inexpensive means of transportation.

##### 2. Chamberlain Region (South Dakota)

This area undoubtedly contains the largest manganese

ore deposits in North America. Unfortunately, they are also of a rather inferior grade. The total deposit averages approximately 1-2 per cent metal content or even less. However, this includes large quantities of shale which enclose nodules averaging 15-17 per cent manganese. A reasonably conservative estimate of the size of the deposit places total reserves at 2.75-3 billion tons or approximately 200,000,000 tons of nodules. Mining costs would be quite inexpensive since most of the ore is in the form of outcroppings, i.e., is near the surface. Estimates of \$.50-\$1.00 per ton do not seem unreasonable. The meaningful figure, however, is that of the cost of the 15-17 per cent manganese concretions. In 1945, this was estimated to be \$3.00 per ton and more recent figures indicate a price tag of \$4.50-\$5.00 per ton. These concretions contain 15-17 per cent manganese and 8-10 per cent iron as carbonates.

Certain geographical disadvantages of this region include the unfavorable climate which would interfere with mining during several months of the year and the long distance to the nearest ferromanganese or steel plant.

### 3. Artillery Peak (Arizona)

These deposits are unique in that they are a wad type ore, and consequently require special beneficiation. The overall size of the deposits has been estimated at 175,000,000 tons. Of this perhaps 5,000,000 tons average approximately 10 per cent manganese with another 15,000,000 tons assaying more than 5 per cent. Most of this ore must be deep mined at a cost of \$4.00-\$5.00 per ton. The vast majority of the ore analyzes between 3.5 and 4 per cent manganese and, depending on the overburden, strip mining costs should lie between \$1.00 and \$3.00 per ton at a daily production rate of 10,000 tons.



It might be well to note that this area in Arizona is extremely hot and arid and almost completely unpopulated. Any sizable installation would necessitate building a complete town. Also transportation charges to either a ferromanganese plant or a steel mill would be high.

B: Silicate Ores and Slags

1. Aroostook County (Maine)

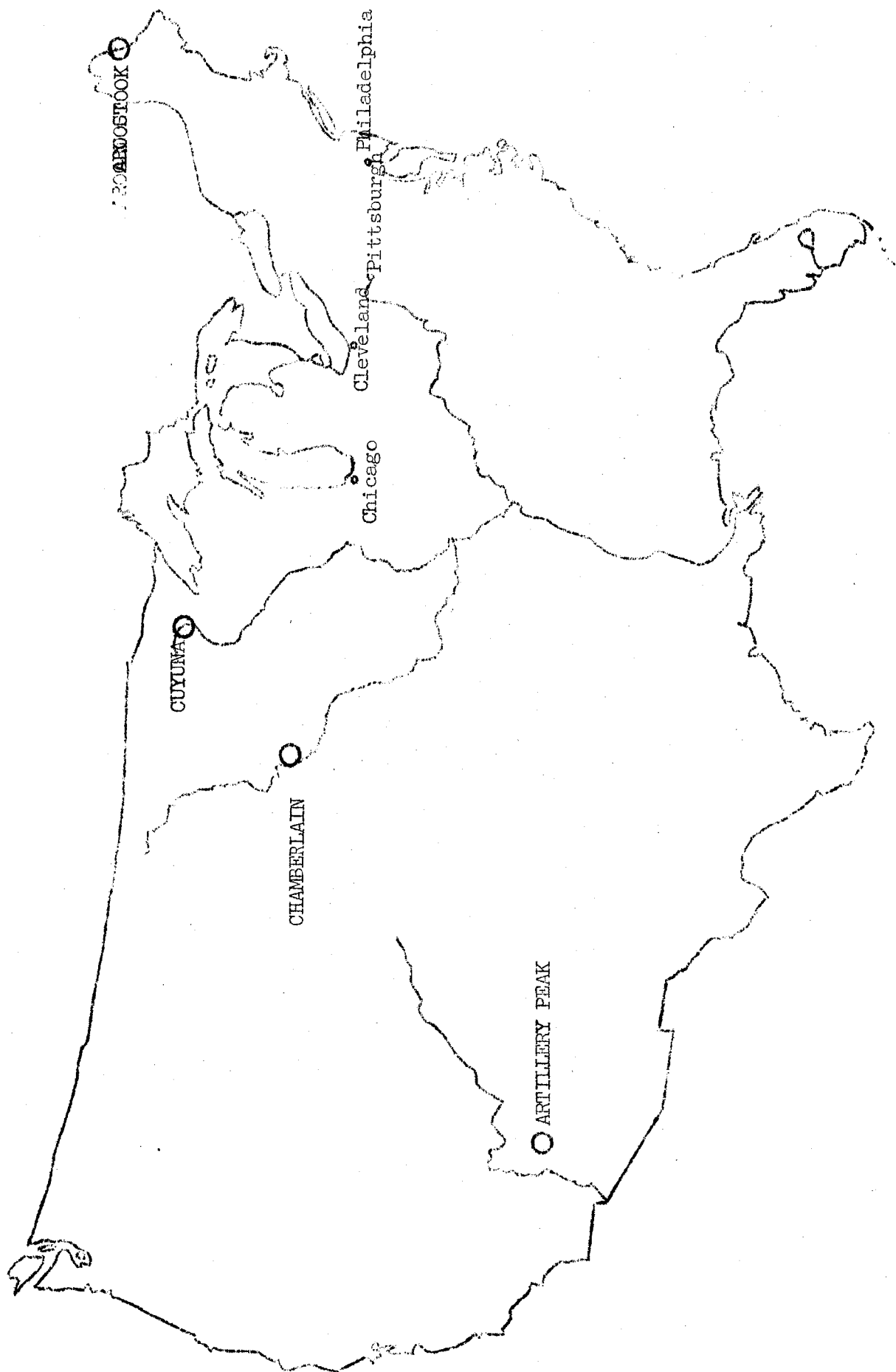
These deposits are huge (perhaps as large as 500,000,000 tons) and, if beneficiated, would probably not be exhausted prior to our iron ore reserves. The ore is very uniform in quality and contains 8-12 per cent manganese. Much of it can be strip mined although the overburden is considerable. A rough guess at mining cost is \$3.00-\$4.00 per ton, depending on the overburden. The two most serious drawbacks to this deposit are:

a. Most of the ores are silicates which are difficult to beneficiate.

b. The location imposes transportation difficulties and severe winters, with their concomitant mining problems, characterize the area.

2. Open Hearth Slags

Approximately 150,000,000 tons of slag with an average of 7 per cent manganese content are stockpiled at various steel plants, and this volume is increasing at the rate of 15,000,000 tons per year. Unfortunately, the flush slags and the lower grade tap slags have not been kept separate and, consequently, the annual slag discard is the more important item. This amounts to approximately 1,100,000 tons of contained manganese. As outlined below in the section treating the Selective Oxidation of Slag-Spiegel (Bureau of Mines),



LOCATION OF MAJOR MANGANESE ORE DEPOSITS

only 900,000 tons of slag are located within feasible shipping distance of the projected recovery plants. Of this quantity 500,000 tons are contained in flush slags averaging 10-12 per cent manganese. One of the biggest obstacles to beneficiating slags is that the manganese is contained in a silicate complex.

This brief survey of the ore deposits and mining methods and costs does not include any estimates of mine "start up" time. This, however, is not a serious omission since even underground mines can be placed in operation within the limits of the gestation period of the simplest beneficiation process listed in this report.

A careful review of the deposit descriptions will indicate that there are three types of ores: silicates, carbonates, and oxides. However, the carbonates can easily be calcined to oxides and, consequently, the division determined by the beneficiation processes are silicate versus non-silicate ores. Three additional comments should be made at this point. First, slags are considered as equivalent to silicate ores; second, the ores at Artillery Peak are wad ores and, although other non-silicate processes would probably be technically feasible, only flotation has a commercial chance of success. Finally, all non-silicates can be treated by the silicate processes; but this procedure would not be economical and, consequently, this possibility will not be considered.

Reserves

Processes

- |                       |  |
|-----------------------|--|
| 1. Cuyuna Range       | All non-silicate beneficiation processes (except flotation). |
| 2. Chamberlain Region | All non-silicate beneficiation processes (except flotation). |
| 3. Artillery Peak     | Flotation, heavy media.                                      |
| 4. Aroostook County   | All silicate beneficiation processes.                        |
| 5. Open Hearth Slags  | All silicate beneficiation processes.                        |

### SECTION III

#### MANGANESE ORE BENEFICIATION PROCESSES

##### A: Oxide and Carbonate Ores

###### 1. Chemical Processes

###### a. Ammonium Carbamate-Carbonate Leach

Perhaps this heading is a misnomer, for, although the most significant process is an ammonium carbamate leach, the other two processes of merit are actually ammonium sulfate leaches, usually followed by an addition of  $\text{CO}_2$  gas to encourage precipitation. Of this group the Dean-Leute process is considered by many as the best beneficiation process for domestic ores which has thus far been developed.

(i) The Bradley-Fitch process was first developed by the Bureau of Mines and has been pilot-planted by the Minnesota School of Mines. The pilot plant has a capacity of 4 tons/day and utilizes Cuyuna Range manganese ore. The samples used were above average grade and assayed 17 per cent manganese, 30 per cent iron, and 30 per cent  $\text{SiO}_2 + \text{Al}_2\text{O}_3$ .

The ore is first crushed and ground to less than 63 mesh and then given a reducing roast. Commercial producers' gas was used as the reducing atmosphere and the temperature was kept at  $750^\circ\text{F}$ . The reduction step is necessitated because only  $\text{MnO}$  is readily soluble in the ammonium sulfate leach liquor. It is also essential that the iron oxides in the ore are not reduced below  $\text{Fe}_3\text{O}_4$  since  $\text{FeO}$  is nearly as soluble in the leach liquor as is  $\text{MnO}$ .

The reduced ore is then sent through a two

stage counter current leaching operation. The leaching reagent is a 10 per cent ammonium sulfate solution which extracts the manganese as a soluble manganese sulfate. This manganese sulfate solution is bled off after the first stage and filtered. The filtrate is pumped to the second leach tank while the concentrated manganese sulfate liquor is sent to an  $\text{NH}_3$  tower where most of the manganese is precipitated out as manganic hydroxide ( $\text{MnHOH}$ ). The precipitation agents are  $\text{NH}_3$  vapor and air. The liquor is then recycled. At the optimal leaching temperature of  $190^\circ\text{F}$ . an extraction of 60 per cent is obtained.

The manganic hydroxide is filtered and then sintered. As an alternative to the last two steps it has been suggested that the manganese might be precipitated as a carbonate if  $\text{CO}_2$  were added to the  $\text{NH}_3$  vapors in the precipitation tower.

Few economic data are available on this process although it appears prima facie to be more expensive than the Dean Process which is described in this section (under iii).

(ii) A process utilizing carbonate ores, but otherwise very similar to the Bradley-Fitch process, has been proposed by A. T. Sweet. The ore is crushed and mixed with ammonium sulfate and then roasted at about  $800^\circ\text{F}$ . This releases  $\text{CO}_2 + \text{NH}_3$  which is condensed in a tower to form an ammonium carbonate solution. This solution is used to precipitate the ore which, in a prior step, has been leached with manganese sulfate.

(iii) However, the process which is generally conceded to be the best of the ammonia leach techniques is the Dean-Leute ammonium carbamate leach. This method of beneficiation has been tested in a small plant by the Manganese Chemical Corporation at Riverton, Minnesota. When using manganese ores such as those of the

Cuyuna Range, it consists of three steps: a reducing roast, a carbamate leach, and an ammonia recovery operation. These are discussed in greater detail below:

Step (a): Selective Reduction

The ore is crushed and fed to a specially designed shaft furnace with a controlled reducing atmosphere of  $H_2$ ,  $CO$ , or commercial producers' gas heated to  $900^{\circ}F$ . Here the metallic oxides are reduced. Since manganese is more easily reduced than iron, a  $MnO$  is produced while most of the iron oxides are reduced only to  $Fe_3O_4$ . This is essential because if the iron oxides are reduced as far as  $FeO$  the carbamate leach is not selective.

Step (b): Ammonium Carbamate Leach

The reduced ore is then fed via an air-tight conveyor belt to agitation tanks. These tanks are steam heated to  $155^{\circ}F$  and contain an ammonium carbamate leach liquor (11-15 per cent  $CO_2$  and 24-28 per cent  $NH_3$ ). The  $MnO$  is selectively dissolved or leached by the liquor while the higher oxides of iron are extracted only slowly. The pregnant liquor (containing manganese-ammonium carbamate complexes) is decanted into a thickener and then pumped to a steam stripper where  $NH_3$  and  $CO_2$  gases are driven off. When about 42 per cent of the  $NH_3$  has vaporized, the manganese precipitates as fine crystals of  $MnCO_3$ . The  $MnCO_3$  is then dried, calcined, and pelletized.

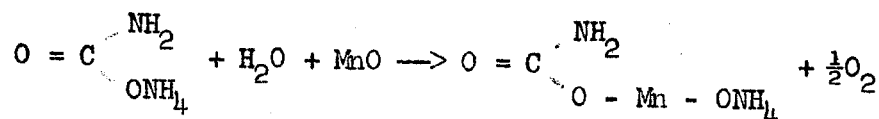
Step (c): Ammonia Regeneration

Here all the  $CO_2$  and  $NH_3$  gases which were stripped off in the tower together with the ammonical liquors are recombined and concentrated via a series of absorbers and scrubbers. Also, make-up  $NH_3$  and  $CO_2$  must be added. The success of the total process is largely dependent on the recovery of  $NH_3$  which is quite expensive. Steps (b) and (c) have been

conducted on a commercial scale by the Manganese Chemical Corporation, but so far the  $\text{NH}_3$  recovery has not approached the 85 per cent which had been anticipated.

Finally, it is advisable to mention a few other pertinent facts here:

(1) The leach mechanism employs a manganese ammonium carbamate complex (see formula) which ultimately precipitates out a  $\text{MnCO}_3$ . The temperature of the leaching tanks is very important since  $\text{MnCO}_3$  will precipitate out at  $250^\circ\text{F}$ . Since the reaction is exothermic, a cooling system may be necessary for larger operations.



(2) The final pelletized product  $\text{Mn}_3\text{O}_4$  analyzes approximately 68 per cent manganese, and the overall manganese recovery approaches 80 per cent.

(3) Singmaster and Breyer have estimated that a plant designed to process 1,280 tons/day of Cuyuna ore (10 per cent manganese) could produce a pelletized product for \$2.09/long ton unit. This cost estimate is predicated on a recovery rate of 78 per cent and a pellet assaying 71 per cent manganese.

- 
1. Production of Manganese from Domestic Sources, Report No. MAB 10-M, Washington, D.C. (1951).
  2. Dean, R. S., Electrolytic Manganese and Its Alloys, The Ronald Press Company, New York (1952).
  3. Sully, A. H., Manganese, Butterworth Scientific Publications, London (1955).
  4. Appraisal of Processes for Recovery of Manganese from Basic Open Hearth Slag, Singmaster and Breyer, New York (1955).
  5. Report of Operations Under Contract DMP-16, Manganese Chemical Corporation, Minneapolis (1956).
  6. Welsh, J. G., personal communication (1956).



## b. Sulfuric Acid and Related Compounds Leach

The sulfuric acid and  $\text{SO}_2$  leaches have been tried in many variations, four of which will be outlined here briefly. All are based on the solubility of  $\text{MnSO}_4$  in  $\text{H}_2\text{O}$  and the use of subsequent evaporation and crystallization step.

(i) The first process to be outlined is the only one that has been tested on a semi-commercial scale. The work was done by the Manganese Ore Company but was never successful because of the formation of metallic thionates.

The process is quite simple although equipment and power costs are rather high. The ore is crushed and then transported to leaching tanks where  $\text{H}_2\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  are added. The  $\text{H}_2\text{SO}_3$  dissolves the higher oxides while the  $\text{H}_2\text{SO}_4$  is necessary to leach the  $\text{MnO}$ . The  $\text{MnSO}_4$  is then evaporated and the crystallized product is sintered and nodulized. If a dithionate,  $\text{MnS}_2\text{O}_6$ , is formed, ring formation results during the sintering step which is necessary to produce  $\text{MnO}_2$  and regenerate  $\text{SO}_2$ .

The Chemical Construction Company (Chemico) and the Battelle Memorial Institute have attempted to circumvent this dithionate obstacle by autoclaving the reacted slurry in the presence of oxygen. This not only eliminates the formation of  $\text{MnS}_2\text{O}_6$ , but also reduces the solution of iron, phosphorus, and the alkali metals. It is also claimed that this will increase the manganese extraction efficiency. The pregnant solution ( $\text{MnSO}_4$ ) is then filtered from the gangue and evaporated to produce  $\text{MnSO}_4$  crystals. These are sintered to  $\text{MnO}_2$ , with the final product assaying 60 per cent manganese. A by-product of the sintering is  $\text{SO}_2$  gas which is absorbed in a tower and recycled. Overall manganese recovery is between 75-80 per cent.

It should be noted that this work was done only in the laboratory using glass equipment. It has the disadvantages of a high temperature and pressure (600 psi) autoclaving step for which extensive use of stainless steel equipment would be necessitated to resist the corrosive action of sulphuric acid.

Battelle has nevertheless estimated that a 300 ton/day plant could produce this high grade ore for approximately \$1.25/long ton unit. This does not include development costs and is predicated on upgrading a 5 per cent Cuyuna ore to a 20 per cent concentrate via a wet mechanism beneficiation process prior to the sulfur leach.

(ii) Another very similar process has been tested by Manganese Products, Inc. and the Continental Chemical Company. In this, instead of an acid,  $\text{SO}_2$  gas is used to leach the  $\text{MnO}_2$  from the manganese ore slurry. During leaching some  $\text{H}_2\text{SO}_4$  is formed and this dissolves any  $\text{MnO}$ . Dithionate formation is prevented by maintaining a relatively high  $\text{O}_2/\text{SO}_2$  ratio in the leaching gas and leaching at a high temperature and low pH. The solution is then filtered and precipitated with  $\text{CO}_2$  or  $\text{NH}_3$ . The  $\text{CO}_2$  addition is not only less expensive but results in a  $\text{MnCO}_3$  precipitate while the  $\text{NH}_3$  yields a precipitate of  $\text{MnHOH}$ . The former is easier to handle and both require sintering before they can be used. This process is now being utilized by Continental to produce high grade battery  $\text{MnO}_2$ .

When  $\text{NH}_3$  is added, an  $\text{NH}_4\text{SO}_4$  by-product is also yielded. The disadvantages of this process are that neither the  $\text{SO}_2$  nor the  $\text{NH}_3$  are recovered and acid proof leaching vessels (stainless steel) must be used.

(iii) Two processes of the Bureau of Mines

should also be mentioned. The first of these is the dithionate process which was pilot planted at Boulder City, Nevada, on a 3 ton/day scale. Artillery Peak ores (9 to 30 per cent) were used. The essential features of the process include: the ore is suspended in a calcium dithionate ( $\text{CaS}_2\text{O}_6$ ) solution and leached with a gas containing  $\text{SO}_2$ . The manganese in the ore dissolves as  $\text{MnSO}_3$  and immediately reacts to form an  $\text{MnS}_2\text{O}_6$  solution and the precipitate gypsum ( $\text{CaSO}_4$ ). The pregnant solution is then treated with lime to precipitate  $\text{MnHOH}$  and regenerate  $\text{CaS}_2\text{O}_6$  which is recycled. The precipitate is filtered and sintered to produce an oxide assaying 60 per cent manganese. An overall manganese recovery of 90 per cent was obtained.

Except for the high reagent costs (since neither the lime nor  $\text{SO}_2$  is recovered) the process is quite attractive. However, approximately 1 pound lime and .75 pound of sulfur are lost in producing 1 pound of manganese. These costs appear to be prohibitive for any large scale commercial operation.

(iv) The other Bureau of Mines process is an  $\text{SO}_2$  roast, research on which is continuing at Minneapolis under Charles Prasky. Development work on this process has utilized carbonate ores from the Cuyuna Range; however, the process should work equally well with oxides.

Essentially, the process consists of three steps:

- (a) A low-temperature roast of the ore
- (b) Treatment with  $\text{SO}_2$  gas and  $\text{H}_2\text{O}$  leach
- (c) Evaporation and calcination.

Since the operation is continuous and the boundaries between steps are indistinct, the entire process will be outlined as a unit.

The crude ore is crushed to less than  $\frac{3}{4}$  inch size (fines are agglomerated to this size) and charged to the top of a shaft furnace. The temperature at the top of the furnace is approximately 900°F. and the ore is calcined here. This step also produces a more porous ore which allows for easier sulfatizing. The sulfatizing occurs as the ore descends in the furnace. The temperature at this step is approximately 1300°F. (the process being exothermic). The actual conversion to  $MnSO_4$  is caused by blowing  $SO_2$  gas and air counter-current to the descending ore. The principal advantages of this process are that the sulfatization is selective for manganese and that no corrosive  $H_2SO_4$  is required.

The treated ore is then discharged and after grinding the  $MnSO_4$  is leached with  $H_2O$ . The  $MnSO_4$  liquor is then thickened in a counter-current decantation system. After final evaporation the  $MnSO_4$  is calcined to produce  $Mn_3O_4$  and  $SO_2$  gas which can be recycled. The  $Mn_3O_4$  analyzes over 60 per cent manganese and an overall recovery for the process of 85-90 per cent has been obtained.

Although earlier tests resulted in a manganese/iron ratio of approximately 25:1, more recent pilot plant tests have been necessary to bring the final product up to the ferro standard of 8:1.

This process is quite attractive for several reasons, including low power consumption due to the exothermic reaction, little corrosion trouble, and recycling of  $SO_2$  gas. Its disadvantages include the high cost of capital equipment and the preliminary calcinating roast.

It has been suggested that this process might be used in conjunction with roasting pyrite to obtain  $SO_2$  and an iron

product. This latter would be mixed with the insoluble shaft furnace residue. Although this scheme would entail a considerably larger capital outlay, it might be more attractive economically. Cost estimates are not available.

- 
1. Production of Manganese from Domestic Sources, Report No. MAB-10-M, Washington, D.C. (1951).
  2. Allen, M. N., "Recovery of Manganese from Low-Grade Ores," Chemical Engineering Progress, 50, 9 (1954).
  3. Prasky, C., "How U.S.B.M. Metallurgists Are Solving the Manganese Shortage," Engineering and Mining Journal, 155, 72 (1954).
  4. Production of Manganese from Domestic Sources, Report No. MAB-71-C, Washington, D.C. (1954).
  5. Sully, A. H., op. cit.
- 

#### c. Nitric Acid Leach

A process which has received much attention and which is still quite controversial is the Nossen  $\text{HNO}_3$  leach. The process is essentially the idea of Dr. Ernest S. Nossen and has been pilot planted at Patterson, New Jersey, on a scale of 12 tons feed/day. Although over \$500,000 has been spent on the project, the results are still somewhat inconclusive and the project is now being evaluated by the Battelle Memorial Institute.

Basically the process involves subjecting the ore to a reducing roast to convert the ore into  $\text{MnO}$  and  $\text{Fe}_3\text{O}_4$  so that the former can be selectively leached with  $\text{HNO}_3$ . However, the Aroostook County ores utilized at the Patterson pilot plant did not require a roast, i.e., presumably the manganese in the treated ores was not contained in a silicate complex.

An ore containing 12 per cent manganese and 18 per cent iron was crushed and ground in a rod mill to approximately 50 mesh and then fed to a stainless steel-jacketed leaching tank. The steam

temperature is kept at about 175° and the leach, a 68 per cent HNO<sub>3</sub>, is pumped in counter-current to the ore flow.

The pregnant liquor (mainly Mn(NO<sub>3</sub>)<sub>2</sub>) is filtered, concentrated in large evaporators, and then sent to a decomposing unit consisting of two large, revolving drums heated to 450°F. A resulting solid product of MnO<sub>2</sub> and some iron and aluminum oxides along with Ca(NO<sub>3</sub>)<sub>2</sub> and some nitrates of sodium, potassium, and magnesium are formed.

This product is ground and leached with H<sub>2</sub>O; the soluble nitrates are filtered off and nitric oxides are regenerated and absorbed in a tower to form HNO<sub>3</sub> which is recycled. The solids remaining from the filter step are primarily MnO<sub>2</sub>. Nitrogen recovery from the nitrate solution reached 90 per cent. The final ore product analyzes 56 per cent manganese (80 per cent MnO<sub>2</sub>) and the process indicates an overall efficiency of 80 per cent.

As far as the economics of the project are concerned, a 640 ton feed/day plant utilizing 11 per cent Mn ores from Aroostook County could, according to Nossen, produce his product for \$1.57/long ton unit. This price includes an ore cost of \$3.93/ton.

An economic analysis calculated to use Chamberlain nodules and the Nossen Process results in a price of \$1.55/long ton unit f.o.b. Chamberlain. This price includes a \$5.43/ton cost of mining and concentrating to a 20 per cent manganese nodule. Perhaps more accurate cost information will be available from the Battelle report.

- 
1. Miller, R. H., MnO<sub>2</sub> from Chamberlain Nodules Via Nossen Nitric Acid Leaching Process, South Dakota Natural Resources Commission (1952).
  2. Beneficiation of Low Grade Manganese Ore from Aroostook County, State of Maine, by the Nitric Acid Cycle Process, Nossen Laboratories, Inc., Patterson (1954).

3. Nossen, E. H., "Beneficiation and Utilization of Manganese Deposits in the United States," Senate Hearings, pp. 99-111 (1955).
  4. Larsen, G. B., personal communication (1956).
- 

d. Hydrochloric Acid Leach

Of all the acid leaches, the hydrochloric (HCl) or the King Process appears, prima facie, to be the least promising. The reasons for this judgment include poor pilot plant recoveries and complications due to the presence of cobalt and nickel in the ores which were utilized. Improvement in these matters would invalidate the "least promising" opinion.

As is the case with most leaching processes, the actual solvent operation is preceded by a reducing roast. The ore is ground to 50 mesh and fed, together with about 10 per cent powdered coke, into a rotary furnace at 1200°F. The manganese is reduced to MnO and the iron, nickel, and cobalt present in the ore are also simultaneously reduced. The ore is then fed into a leach tank containing HCl and the reduced ore dissolves out as metallic chlorides. The pH of the solution is then raised and a blast of air through the filtrate solution hydrolyzes the iron to Fe(OH)<sub>3</sub>. This is then filtered out and H<sub>2</sub>S is added to this filtrate to precipitate out the cobalt and nickel as sulfides. Any excess sulfur from the H<sub>2</sub>S is removed by the addition of some FeCl<sub>3</sub> which precipitates the H<sub>2</sub>S out as FeS. The manganese is recovered by adding CO<sub>2</sub> to the remaining solution to yield the precipitate MnCO<sub>3</sub>.

This process has been tested by Dr. King in a 12 ton/day pilot plant. Unfortunately, the operation was not too successful and the manganese recovery fell below 50 per cent. Nevertheless, many engineers feel the process has not been given an adequate test run

and that the efficiency can be greatly increased.

The economics are quite involved and by-product income is essential even to approximate commercial feasibility. Dr. King's own estimate was approximately \$3.00 per long ton unit for a pure  $MnCO_3$  even with some by-product credits. Due to the availability of some excess HCl in Ohio, the Food Machinery Corporation is seriously considering commercial manganese production via this process. While the primary motivation is the expected supply of cheap HCl, the Food Machinery Corporation hopes to circumvent most of the difficulties arising from the impurities by utilizing an ore whose nickel and cobalt contents are low.

- 
1. King, L. W., "Beneficiation and Utilization of Manganese Deposits in the United States," Senate Hearings, pp. 138-145 (1955).
  2. Larsen, C. B., States of Research Projects for Upgrading Sub-Metallurgical Manganese Ores and Slags, General Services Administration (1956).
- 

#### e. Electrolysis

At present, less than 2 per cent of the total manganese consumed is utilized in the form of metallic (electrolytic) manganese. The reason for this is its prohibitive cost incurred by complicated processes which consume large quantities of electric power. Approximately 25,000 tons of metallic manganese and manganese dioxide are being commercially produced. The manganese metal processes utilize high grade imported ores as input while the manganese dioxide used for battery purposes consumes 20 per cent manganese domestic ores.

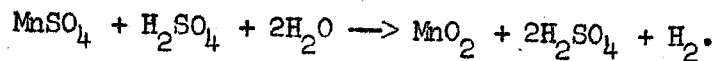
Essentially the processes are similar to the sulfuric acid leach (possibly preceded by an ammonium carbamate leach) with the spent electrolyte serving as the leaching agent. After the



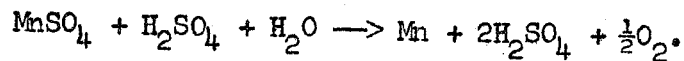
MnSO<sub>4</sub> solution is purified as outlined in the sulfuric acid leach description, the solution is pumped to an electrolytic chamber where manganese is plated out. Consequently, the only additional cost to produce the metal from the upgraded ore is electric power which would probably exceed \$.50/long ton unit.

Because all electrolytic processes are essentially the same, only the Schumacher process will be outlined here. The ore is crushed and milled to 20 mesh and then given a reducing roast (at 1400°F.) to convert to MnO. The reduced ore is then leached with the spent electrolyte (H<sub>2</sub>SO<sub>4</sub>) at 140°F. (pH 3-3.5). Then, to increase settling of heavy metal sulfides, BaS and CaO are added; an aeration oxidation and filtration step remove the iron. The pH of the MnSO<sub>4</sub> solution has at this point reached 7.2-7.5 and is pumped into an electrolytic chamber.

In the Schumacher process, MnO<sub>2</sub> is desired and it is plated out on a graphite anode as shown:



When Mn metal is desired plating takes place at a stainless steel cathode according to the following equation:



The best power estimates approach 2,000 kwh/ton of metallic product. The capital outlay for a 25 tons/day plant would be \$7,300,000. Even the most optimistic estimates for large scale metallic manganese production yield a total cost over \$3.00/long ton unit.

- 
1. Jacobs, J. H., Electrowinning of Manganese from Domestic Ores, Bureau of Mines Report of Investigation 4163 (1947).
  2. Dean, R. S., Electrolytic Manganese and Its Alloys, The Ronald Press Company, New York (1952).
  3. Schrier, E., and Hoffmann, R., "From Low Grade Domestic Ores: High Grade Manganese Dioxide," Chemical Engineering, 61, 152 (1954).

## 2. Physical Processes

### a. Flotation

This process is not only a well known and tested mineral beneficiation process but has been and is being utilized on a commercial scale in this country. In fact, of the 300,000 tons of ferrograde manganese ore produced domestically in 1955 over 200,000 tons were produced by two corporations, both of which upgraded these ores via a flotation process.

Both these corporations, however, utilize selective ores. Anaconda floats manganese as a by-product of zinc, copper, and silver ores, while Manganese, Inc. utilizes a 20 per cent manganese ore at Three Kids. This latter deposit is being exhausted and a lower grade ore will presumably have to be used. Manganese, Inc. has supplied the project with estimates for utilizing Artillery Peak ores.

The flotation process utilized by both the United States Bureau of Mines on Artillery Peak ores and by Manganese, Inc. at Three Kids involves three steps:

- (a) Grinding
- (b) Flotation
- (c) Sintering

#### Step (a): Grinding

This, of course, is almost self-explanatory. The ore which may be either surface or deep mined, is first crushed and then ground to a 100-200 mesh size. This is a very sizable operation, considering the low grade ore and the particle size desired.

#### Step (b): Flotation

The ground ore is then fed into the flotation chamber. The reagents are absorbed by the manganese ore, causing it to float to the

top; this ore-bearing solution can then be decanted. The gangue does not float (tailings) and is drained from the bottom of the tank. According to the Bureau of Mines, the reagent requirement for the Artillery Peak ores include 10 pounds soap, 12 pounds oil, and 2 pounds wetting agent/ton of ore. However, Manganese, Inc., using a much more absorbent ore, used roughly 50, 120 and 8 pounds/ton ore of soap, oil, and wetting agent respectively. Since the reagent expense is one of the largest cost items of the process, this is quite important. These decreased reagent costs may offset the additional handling and grinding charges of the lower grade Artillery Peak ores (9 per cent, as compared to Three Kids 20 per cent). The recovery by this step is easily 85 per cent, with a final manganese content of 35 per cent.

#### Step (c): Sintering

This 35 per cent manganese ore can be upgraded to meet ferromanganese specifications by sintering. The sintering can be accomplished via a sintering machine or, on a larger scale, a rotary kiln. The overall recovery of the process is about 75 per cent.

The actual cost of a ferro-grade ore obtained in this manner at Three Kids is substantially less than the normal government purchase price of \$2.30/long ton unit.

- 
1. Havens, R., Potter, M. C., and Hussey, S. J., Concentration of Oxide Manganese Ores from the Artillery Peak Deposit, Mohave County, Arizona, Bureau of Mines Report of Investigation 4148 (1947).
  2. West, H. S., "Beneficiation and Utilization of Manganese Deposits in the United States, pp. 73-83, Senate Hearings (1955).
  3. Adkerson, J. C., personal communication (1956).
  4. McGonigle, F. A., private communication (1956).
  5. McGonigle, F. A., personal communication (1956).
- 

#### b. Heavy Media Separation and Tabling

These are actually two quite distinct methods of

beneficiation but are frequently used together in successive steps to concentrate manganese ores. Another reason for their common grouping is their relative unimportance when used as the sole means of mineral dressing. This statement is predicated on the fact that these combined steps cannot generally raise the absolute manganese content by more than 10 or 20 per cent, and even this upgrading is obtained at the expense of low recovery. Thus, their usefulness appears limited to extensive deposits of a 20 per cent manganese ore. These, of course, if existent, have not yet been discovered in the United States.

Heavy medium separation is based on the relative density of the metal (element or compound) compared to that of the gangue. The ore is crushed to less than 2 mesh. The 2-10 mesh size is then dumped into a tank into which a galena solution (specific gravity = 3) is pumped. The gangue, which is the lighter element, is floated off, leaving a tailing of high manganese concentration.

The middling from this operation, together with the less than 10 mesh ore, is tabled. Tabling is simply moving a finely ground ore across a plane surface. The ore is guided by cleats and the necessary motion is provided by shaking. A spray of water is shot at a right angle to the cleats and carries away the gangue, while the heavier mineral continues to move in the direction of the cleats.

---

1. Bureau of Mines Reports of Investigations (too numerous to specify).

---

### c. Crushing and Jigging

As is the case with heavy media separation and tabling, these methods of upgrading ores are usually regarded as ore dressing techniques rather than beneficiation processes. Their

inclusion in this report can only be justified on the basis of their utilization as preliminary steps for other beneficiation processes, e.g., the Nossen process on Chamberlain ores.

Crushing is self-explanatory and varies primarily due to the size of the particle desired. This, of course, necessitates various types of machinery, from simple sledge hammers to large gyratory crushers.

Jigging is quite simple and consists essentially of shaking a raw ore and separating out the hard ore from the gangue by washing and classifying. This, too, can be done via a simple box or a large grizzly screening machine.

## B. Silicate Ores and Slags

### 1. Pyrochemical Processes

#### a. Lime Clinkering (Sylvester)

This process was originated in the laboratories of Sylvester and Company, a private research organization, and has been pilot planted (small scale) by the United States Bureau of Mines at College Park. The General Services Administration is considering financing a large scale test run and in 1955 nearly entered an agreement to spend \$650,000 to test this process.

Basic open hearth slag or silicate ore and limestone ( $\text{CaCO}_3$ ) are crushed to less than  $\frac{3}{4}$  inch and mixed in the ratio of 3.4:1 or the necessary proportions to yield a molar  $\left(\frac{\text{CaO}-3\text{P}_2\text{O}_5}{\text{SiO}_2}\right)$  ratio of between 1.5 to 2.2. This mixture is charged into two successive rotary kilns. In the first kiln, which is heated to  $2400^\circ\text{F}$ ., the limestone is calcined, while in the second kiln the charge is slowly cooled to  $2100^\circ\text{F}$ .. During this latter interval the manganese silicate bond of the slag is broken and a clinker consisting of two phases is produced. The

first is a spinel of manganese, iron, aluminum, and magnesium oxides, while the other phase is a dicalcium silicate containing the phosphorus. This product is then pulverized (40 mesh) and the metallic oxide phase is removed via magnetic separators.

There are, however, some real drawbacks to the process. Perhaps the most important is the limited amount of upgrading. The magnetic concentrate weighs  $\frac{3}{4}$  as much as the original ore and, even assuming a 100 per cent recovery, this would hardly increase the manganese content by more than 4 or 5 per cent. Also, the process does not differentiate between iron and manganese and no improvement in this critical ratio can be expected. The cost of the operation is estimated at \$10/ton of concentrate, but the final product is little more than a low grade spiegel.

The merit of the process is that it converts silicates into oxides, and thus allows for further treatment (e.g., via the Dean process).

- 
1. Ruppert, J. A., Manganese Concentrates from Open Hearth Slags by Lime-Clinkering (Sylvester) Process, Bureau of Mines Report of Investigation 4847 (1952).
  2. Heindl, R. A., Ruppert, J. A., Skow, M. A., and Conley, J. E., Manganese from Steel Plant Slags by a Lime Clinkering and Carbonate Leaching Process, Bureau of Mines Reports of Investigations 5124 and 5142 (1955).
  3. Sylvester, G. R., and Cole, R. S., "Beneficiation and Utilization of Manganese Deposits in the United States, Senate Hearings, pp. 227-245 (1955).
- 

b. Lime Clinkering-Carbamate Leach (Sylvester-Dean)

Although this process has never been treated in its entirety, it paradoxically is one of the most technically promising and most tested operations. Also, its economic aspects commend it. This process also utilizes slags and, consequently, everything which has been

said about slags previously, especially concerning the availability of flush slags, is applicable to this process also. It should be noted that the cost estimates to be reported later will be based on the use of flush slag.

Essentially this beneficiation process consists of four steps which are:

- (a) Lime-Clinkering
- (b) Selective Reduction
- (c) Carbamate Leaching
- (d) Ammonia Regeneration

Step (a) has been completely outlined in the preceding section (Sylvester); steps (b), (c), and (d) have been described under the Ammonium Carbamate-Carbonate Leach section, subdivision (iii), the Dean-Leute process. The first two steps have been successfully conducted by the Bureau of Mines at College Park, utilizing a sintering machine and a 3 by 30 feet rotary kiln for step (a) and a rabble furnace 42 by 62 inches for step (b). This allowed a feed of 2 tons slag/day. Although the Bureau of Mines also pilot planted a process to leach this reduced slag with an ammonium carbonate solution, it is felt that the work of the Manganese Chemical Corporation with an ammonium carbamate leach offers a sounder basis for consideration.

Singmaster and Breyer have estimated that the final product, a  $Mn_3O_4$  pellet, can be produced for \$1.95 per long ton unit. These figures are based on slag (including freight) at \$2.00 per ton and an overall manganese recovery from the slag of more than 80 per cent. According to the Bureau of Mines, this is not an unreasonable estimate. A recovery of more than 80 per cent would also indicate that almost 40 per cent of the manganese alloy needs could be supplied from

flush slags if this process were utilized. Another pertinent factor is its low capital expenditure as compared to the pyrometallurgical methods.

- 
1. Heindl, R. A., Ruppert, J. A., Skow, M. L., and Conley, J. E., Manganese from Steel Plant Slags by a Lime-Clinkering and Carbonate Leaching Process, Bureau of Mines Reports of Investigations 5124 and 5142 (1955).
  2. Appraisal of Processes for Recovery of Manganese from Basic Open Hearth Slag, Singmaster and Breyer, New York (1955).
  3. Report of Operations Under Contract DMP-16, Manganese Chemical Corporation, Minneapolis (1956).
  4. Heindl, R. A., personal communication (1956).
  5. Conley, J. E., personal communication (1956).
  6. Welsh, J. Y., personal communication (1956).
  7. Welsh, J. Y., private communication (1956).
- 

#### c. Chlorine Vaporization

The chlorine vaporization processes were first proposed by private industry (Armco and U.S. Steel), and limited laboratory research has been conducted by the United States Bureau of Mines and the Armour Research Institute. Unfortunately, the experimental work has not advanced far enough to make any meaningful cost estimates.

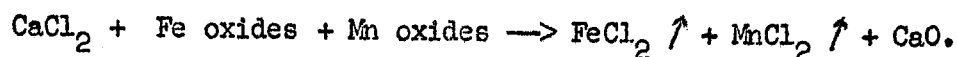
Actually there are two processes, the  $\text{CaCl}_2$  and the gaseous HCl. Although  $\text{CaCl}_2$  is an inexpensive chemical, the cyclic nature of the HCl process gives it a materials advantage. This is especially important because of the fact that 2 to 3 times the stoichiometric requirement of chlorine seems necessary to extract efficiently the manganese in the ore or slag. Another important factor favoring the HCl process is the space velocity bottleneck. The gas not only speeds up the reaction, but also can be used to sweep, thus lowering the pressure. This allows an efficient reaction at a lower temperature. Unfortunately, this superiority is attained at the price of increased



corrosion difficulties and additional equipment necessary for the recovery of the HCl gas.

The data included in this report are obtained primarily from the work of the Bureau of Mines at College Park. In this research, Aroostook silicate ores were used. However, since the manganese and iron contents of slags are quite similar, it appears logical that these results could also be applied to slags.

In the  $\text{CaCl}_2$  process the basic reaction is given by the equation:



The recovery of manganese is dependent on three major factors: 1) the ratio of  $\text{CaCl}_2$ /ore, 2) temperature, and 3) reaction time. It is felt that the optimum feed ratio is 0.7 and that  $2000^\circ\text{F}$ . is the best temperature. However, to obtain 90 per cent recovery of the manganese requires a reaction time of three hours in the tube furnace used. This large reaction time is the major shortcoming of the process and if the process is to become commercially feasible, it must be drastically reduced. Under these conditions 40 per cent of the iron is also volatilized and the resulting 3 or 4:1 manganese/iron ratio does not meet ferromanganese ore specifications.

Unfortunately, these two problems also apply to the gaseous HCl process. In this case the HCl gas is forced up through the ground slag (48 mesh) in a shaft furnace heated to  $1700\text{-}1800^\circ\text{F}$ . This counter-current operation also requires 2 to 3 times the stoichiometric requirement of HCl gas and the reduced temperature (largely due to sweeping the system with HCl gas) does not seem to increase the volatilization of manganese relative to iron. The space velocity of the volatilization reaction is, again, inordinately high. At present, the

Bureau of Mines is trying to solve this problem by fluidizing the reactants (65-200 mesh) and including the coke directly in the charge.

The most efficient method of recovering the volatile chlorides is by hydrolysis (steam at 1100-1250°F.). This yields manganese and iron oxides as products along with HCl and H<sub>2</sub>O. The HCl and H<sub>2</sub>O mixture is then sent to a scrubbing tower where the HCl is reclaimed and recycled. The total HCl efficiency is approximately 80-85 per cent. One of the principal shortcomings of the HCl system is the corrosion problem induced by the gaseous HCl; any water vapor present aggravates this situation. Thus far, no satisfactory solution has been found to this problem.

It has also been shown that the manganese/iron ratio can be increased up to 40:1 by selectively hydrolyzing the iron from the chloride product. This necessitates successive recycling steps.

- 
1. MacMillan, R. T., and Turner, T. L., Recovery of Manganese from Ores of Aroostook County, Maine, Bureau of Mines Report of Investigation 5082 (1954).
  2. MacMillan, R. T., personal communication (1956).
  3. Turner, T. L., personal communication (1956).
  4. Conley, J. E., personal communication (1956).
- 

d. Chemical Roasting (Bruce Williams)

This process has received favorable attention due to its applicability to silicate ores and slags. These are ground together with certain chemicals (the identity of which has not been revealed) and roasted. This product is leached with H<sub>2</sub>O and presumably the solution is treated with CO<sub>2</sub> and perhaps NH<sub>3</sub> to precipitate out the manganese as MnCO<sub>3</sub>. The other reagents are recovered and recycled.

Though not much is known about the process, it appears similar to the other roasting-leaching methods. Its feasibility depends on both the efficient recovery of the manganese and the success in recycling the unknown chemicals. If successful, it should rival the Sylvester-Dean process.

This process is being pilot planted by Ores Beneficiation, Inc. and data should be available by February 1957.

---

1. Larsen, C. B., Status of Research Projects for Upgrading Sub-Metallurgical Manganese Ores and Slag, General Services Administration (1956).

---

2. Pyrometallurgical Processes

a. Selective Oxidation of Slag-Spiegel (Bureau of Mines)

Despite its obvious drawbacks as an emergency method of production of manganese due to its utilization of much coke and blast furnace capacity, this process is looked upon with considerable favor by influential people in the steel industry and the Bureau of Mines. Perhaps this attitude can be explained by the fact that the pyrometallurgical treatment is simply a new application of conventional practices with which these circles are quite familiar. Also, the ready and visible availability of slags may be partially responsible for this stand. Moreover, the process may also be applicable to silicate ores.

In any event, the consequences of its favorable position are quite real, as a very extensive research and development program has been completed, and a thorough engineering cost estimate has been made. These projects have been supported both by the Federal Government through the Bureau of Mines and private industry via the

American Iron and Steel Institute.

The technology of the process has been well proven through pilot plant studies utilizing a 3-foot diameter blast furnace at Pittsburgh. And despite the failure of the semi-commercial Mangaslag plant at Pittston, Pennsylvania, there is little doubt of the technical feasibility of the process.

The most promising proposal for the pyrometallurgical treatment of slags consists of a four-stage process:

(a) Smelting of the open hearth slag in a blast furnace to produce a high phosphorous spiegeleisen.

(b) Selective oxidation of the spiegeleisen in a basic side blown converter to produce a high manganese content slag and also a high phosphorous iron.

(c) Production of ferromanganese in a blast furnace from the synthetic manganese ore or slag.

(d) Dephosphorization of the iron by-product of the spiegel oxidation of (b) in a basic side blown converter.

Each of these steps will be briefly outlined here with the emphasis on inputs, outputs, and recovery.

Step (a): Smelting of Open Hearth Slags in the Blast Furnace:

Perhaps the most dependable data are those obtained in the U. S. Bureau of Mines' most recent report of work conducted in July 1955 on a 3-foot diameter furnace. The daily charge to this furnace was approximately 30 tons. The charge included open hearth flush slag, coke, limestone, and dolomite. The slag/coke ratio averaged 1.51 while the slag and flux/coke ratio averaged 1.91. The average manganese content of the flush slag was just under 10.5 per cent. The product was a spiegel averaging slightly less than 20 per cent manganese for a

recovery of approximately 65 per cent.

The slag utilized in these experiments, although representative as far as the manganese content is concerned, was definitely acidic and consequently required a relatively large flux ratio. The slag analyzed .84 basicity  $(\text{CaO} + \text{MgO})/(\text{SiO}_2 + \text{Al}_2\text{O}_3)$ , whereas an average slag from the four largest steel districts would run above 1.00 basicity with the Eastern district as high as 1.24. As originally planned, the first step would be a non-flux operation and, although this may not be possible, the normal flux ratio should be considerably lower than that stated above. The air blast temperature was 2130°F.

Step (b): Selective Oxidation of the Spiegeleisen:

This operation consists of blowing the spiegeleisen from step (a) in a basic lined side blown converter. The spiegel analyzes approximately 18-20 per cent manganese, 1-3 per cent silicon, 2-4 per cent phosphorus, 2-3 per cent carbon, and 70 per cent iron. The selective oxidation process is designed to oxidize the manganese into a slag without simultaneously oxidizing the iron and phosphorus. At first this could be done only by utilizing short blasts, which resulted in an inefficient manganese recovery. However, the Bureau of Mines devised a cyclic process for greater manganese recovery which yielded the following slag product: manganese 53-57 per cent, phosphorus .03-.18 per cent, iron 5 per cent, and  $\text{Si}_2\text{O}_3 + \text{Al}_2\text{O}_5$  15 per cent. Only the acid oxide ( $\text{Si}_2\text{O}_3 + \text{Al}_2\text{O}_5$ ) content fails to meet the specifications for manganese ore for ferromanganese production. It should be noted that the high silica content is not due to the original silicate composition of the open hearth slag but to the addition of ferrosilicon in the converter. This addition is necessary to impart sufficient fluidity to the viscous slag product to prevent it from entrapping phosphorus

particles. The most significant characteristic of the blowing operation is that the manganese content of the spiegel (15-23 per cent) does not seem to determine the percentage of manganese in the synthetic ore (converter slag). From this one infers that except for the additional heating burden (coke) tap slags could also be used as a "raw material" especially if silico manganese is the desired end product.

A by-product of the converter step is an iron analyzing 3 per cent phosphorus, 1 per cent carbon, and 1 per cent manganese. The recovery of both the iron and manganese in their respective processes is approximately 90 per cent.

Step (c): Production of Ferromanganese from Synthetic Ore:

This process is, of course, in large scale commercial operation with foreign ore (see Section IV). The converter slag would be treated in a similar fashion but would receive a credit due to its excellent analysis, i.e., high manganese content, and low iron and phosphorus percentages.

Step (d): Dephosphorization of the Iron By-Product of the Spiegel  
Oxidation

The metal is poured into a second converter and sufficient lime (CaO) is added to reach a ratio of 3:20 CaO/metal. The air blast temperature is kept at 2850°-2950°F., to oxidize selectively the phosphorus from the iron metal. The resulting products include an iron containing less than .25 per cent phosphorus which is cast into small ingots and sold at a high (resale) price, and a  $\text{CaO} \cdot \text{P}_2\text{O}_5$  slag containing less than 5 per cent iron, 10 per cent  $\text{SiO}_2$ , 5 per cent MgO, and 2 per cent manganese. The phosphate product is 95 per cent soluble in 2 per cent citric acid, which is the standard test used by agricultural chemists. Also, it should be noted that the blowing did not appreciably

increase the nitrogen content of the iron.

Availability of slags(1953): The steel industry consumes annually approximately 1,000,000 tons of manganese metal as alloy additions. At the same time, it discards 1,100,000 tons of manganese to open hearth slag dumps. (Most of this manganese is introduced via manganese bearing iron ore and scrap.) Of this amount perhaps as much as 900,000 tons are located within feasible shipping distances of the five most frequently proposed plant areas, i.e., Pittsburgh, Chicago, Cleveland, Youngstown, and Eastern. However, of this amount only 5,000,000 tons of manganese are contained in flush slags while the remaining is tap slag. Even assuming a 55 per cent recovery for the combined operations (spiegel, selective oxidation, and ferromanganese manufacture) for flush slags and 50 per cent for all slag, this would result in 275,000 and 450,000 tons of manganese obtained respectively from flush slag and total slag. This, of course, is equivalent to, respectively, 27.5 per cent and 45 per cent of the total industry needs.

The economics of this process are quite complicated. Singmaster and Breyer's report indicates for the so-called "synthetic ore" a cost of approximately \$3.40/long ton unit. This figure is based on a selling price for the dephosphorized iron, the so-called "steel scrap", of \$32.50/ton; the \$3.40 cost includes also \$2.00/ton shipping charges for slags, which seems high. If, however, a \$59.60/ton price were used for the "steel scrap" and \$.75/ton for transportation charges, as suggested by Mr. Royster, the cost of the "synthetic ore" would approach \$2.40/long ton unit. This figure is still high compared with those of other processes, which is due to the large capital expenditures of the necessary "steel mill" equipment.

- 
1. Economic Evaluation of the Pyrometallurgical Process of the Bureau of Mines on the Recovery of Manganese from Open Hearth Slags, Arthur G. McKee and Company, Cleveland (1954).
  2. Buehl, R. C., Dephosphorization of the Phosphor-Iron By-Product of Spiegeleisen Oxidation in the 2,000 Pound Basic Side Blown Converter, Progress Report BM-AISI (1954).
  3. Royer, M. B., and Buehl, R. C., Manganese Recovery from Open Hearth Slags by Reduction in a 36-Inch Hearth Experimental Blast Furnace and Oxidation in a 1-Ton Basic Converter, Progress Report BM-AISI (1955).
  4. Royster, P. H., Production of Ferromanganese from Steel Plant Slag by the Selective Reduction Process, Washington, D.C. (1955).
  5. Appraisal of Processes for Recovery of Manganese from Basic Open Hearth Slag, Singmaster and Breyer, New York (1955).
  6. Royster, P. H., Ferromanganese from Steel Plant Waste Slag, Bureau of Mines memorandum, Washington, D.C. (1956).
  7. Royster, P. H., personal communication (1956).
  8. Royer, M. B., personal communication (1956).
- 

b. Electric Furnace Reduction (Udy)

This process differs from most of the other processes in that it does not produce a synthetic ore, but instead yields either a low grade silicomanganese or a standard grade ferromanganese. Although not much information is yet available on the process, it will be briefly and tentatively outlined.

New Brunswick ores analyzing 11 per cent manganese and 13 per cent iron combined as silicates are crushed and fed into an oil field furnace where they are melted. The molten ore is then transferred to an electric furnace where it is reduced with coke or ferro-silicon. The iron and the slag, which contains 30 per cent manganese, are separated and the slag is funneled into a second furnace and further reduced to a standard grade ferromanganese.

So far, few data are available. However, a 50 ton/day prototype plant at Niagara Falls has just begun operations and information has been promised when it becomes available early in 1957.

This process is being privately developed by the



Strategic Materials Corporation which plans to build a plant to produce 75,000 tons of ferromanganese/year. Impartial security analysts have predicted large profits for the operation. Income per ton of ferromanganese is set at \$225 plus a \$45 credit for the by-product iron. Operating expenses including high power costs have been estimated at \$150/ton and interest and amortization would cost another \$30. This would yield a net profit of \$90/ton. If these figures are correct, then this process is a very significant factor in the manganese picture since the New Brunswick ore deposits and the neighboring Aroostook deposits are extremely large.

- 
1. Forbes Special Situation Survey, New York, February 17, 1956.
  2. Larsen, C. B., Status of Research Projects for Upgrading Sub-Metallurgical Manganese Ores and Slags, General Services Administration (1956).
  3. Udy, M. J., private communication (1956).
- 

#### c. Selective Oxidation of Pig Iron (Wright)

The inclusion of this process under silicate ores and slags is rather arbitrary. It is a complicated and controversial process — a process which must be integrated into actual steel mill production — a process which utilizes a 4-5 per cent manganese containing iron ore — a process whose end product, a slag containing less than 40 per cent manganese, is of doubtful utility — yet it is not only fascinating and technically feasible but perhaps is even commercially profitable.

The idea of the process is largely that of Professor E. C. Wright of the University of Alabama, and some small scale experimental work has been conducted there in cooperation with Union Carbon and Carbide. It has also been favorably studied and

analyzed by the Battelle Memorial Institute.

Essentially, the process consists of feeding high manganese content iron ores (Cuyuna Range) into the blast furnace. An alternative is to raise the manganese content of the furnace charge by the addition of some open hearth slag. The intent is to produce a hot metal pig analyzing 4-5 per cent manganese. This would necessitate the addition of more flux to counteract the additional silica resulting from the new ore mix and also an increase in coke due to the higher temperatures demanded by the increased manganese content of the blast furnace burden.

The resultant hot metal pig is transferred to a side blown converter (silica lined) and blown to oxidize selectively the manganese into a slag analyzing 50 per cent MnO, 8 per cent FeO, and 42 per cent SiO<sub>2</sub>. The remaining superheated pig which has been partially desiliconized (but which contains a bit more phosphorus) is then charged into the open hearth furnace to be made into steel.

The success of this process is largely dependent on the ultimate disposition of the manganese slag which closely resembles rhodonite. If commercial ferro and silicomanganese producers can utilize it, or if the Udy (Strategic Materials Corporation) process proves successful, then there appears to be a real future for the bessemerizing of high manganese pig iron. The most likely possibility is the direct processing of the slag to a standard grade silicomanganese.

Professor Wright estimates the cost of this synthetic ore at approximately \$1.45/long ton unit. It should be noted that this does not include a credit for superheating or desiliconizing the open hearth charge (by-products of the bessemerizing). The fact that the process utilizes blast furnace capacity, which most likely

would be short in an emergency period, must be considered.

Also, since it affects the entire steel making process, its biggest obstacle is to overcome the difficulties presented by a large investment and other resistances to innovation, which may be considerable in an industry not marked by a high degree of technological change.

- 
1. "Manganese Recovery from Basic Iron," Resources for Freedom, Vol. IV, pp. 52-53, Washington, D. C. (1952).
  2. Wright, E. C., "Recovery of Manganese in Steel Mill Operations," presented at the Birmingham Regional Meeting of the American Iron and Steel Institute, October 21, 1953.
  3. Wright, E. C., private communication (1956).
- 

### 3. Physical Processes:

#### High Intensity Arc

Research on this process has not advanced enough to yield any economic data. However, the Vitro Corporation, under contract with the General Services Administration, is now pilot planting the process and has promised some data early in 1957.

Essentially, the process consists of intensifying a heat concentration which raises the temperature to the 13,000<sup>o</sup>-18,000<sup>o</sup>F. range. This results in a flash evaporation of the metal and the resulting vapors (which in this case are a manganese oxide) are condensed and then leached by a commercial solvent.

The high temperature is reached by substituting for the conventional carbon anode an electrode of 80 per cent rhodonite and 20 per cent coke (carbon). Thus, additional energy beyond the normal arc temperature of 7000<sup>o</sup>F. is used to dissipate the electrode (vaporize the ore). This process is especially significant in that the silicate ore, rhodonite, can be utilized.

The economics of the project look somewhat promising at first glance, but the necessity of a second step (leaching) may increase cost beyond the savings gained by utilizing a high grade 35 per cent rhodonite. This is a domestic ore available in sizable quantities, particularly in Colorado.

- 
1. "Metals from a Flaming Arc," Chemical and Engineering News, 34, 1332 (1956).
  2. Larsen, C. B., Status of Research Projects for Upgrading Sub-Metallurgical Manganese Ores and Slags, General Services Administration (1956).
  3. Larsen, C. B., personal communication (1956).
  4. Little, E., private communication (1956).
-

## SECTION IV

### ALLOY PRODUCTION METHODS

This supplement to a report which is concerned primarily with the beneficiation of low grade domestic ores is considered necessary for two reasons:

(a) Several of the processes described are fully integrated to manufacture ferro, silico, or metallic manganese.

(b) More than 90 per cent of all the manganese ore consumed in this country is as a ferro or silico alloy. Consequently, a valid comparison of these processes should consider the end product as well as the intermediate item.

In 1956, ferromanganese production completely outstripped the production of silicomanganese, but a trend towards the increased use of silico is quite evident. Ferromanganese is produced both via the electric furnace and the blast furnace, while the silico alloy is manufactured only in the former. These processes will be considered separately.

#### A. Ferromanganese

##### 1. Blast Furnace

The production of ferromanganese involves only the standard metallurgical reducing operation. A ferrograde manganese ore, which contains manganese and iron in the form of oxides, is reduced with coke to an alloy analyzing 78-80 per cent manganese, 13 per cent iron, and 6-7 per cent carbon. In order to obtain this final product the feed ore must meet certain specifications. These are known as the

standard ferrograde manganese ore specifications, which require that the ore contain at least 40 per cent manganese (although 46-48 per cent is more frequently suggested), a minimum manganese/iron ratio of 8:1, and a maximum silica requirement of 10 per cent. Since phosphorus is detrimental to steel production, it is also limited to a .2 per cent maximum. These specifications are not arbitrary but explain the peculiarities of the process.

For instance, the ferromanganese product has a manganese/iron ratio of 6:1, whereas the ore specification is 8:1. The reason for this is that manganese has a much higher affinity for oxygen than does iron, and consequently, whereas the recovery of iron charged is virtually complete, only 80 per cent of the manganese is recovered. This high oxygen affinity also explains the differences in the mode of operation of blast furnaces used for pig iron production and those used for ferromanganese. While the reduction of FeO is exothermic, the reduction of MnO is endothermic and, consequently, the coke consumption is greatly increased. Approximately 2-3 tons of coke are required to produce one ton of ferromanganese, while only .75 ton coke is required to make one ton of pig iron. This greater oxygen affinity also precludes reduction in an atmosphere containing only small amounts of CO<sub>2</sub>; thus all smelting must take place where the manganese is in contact with solid carbon or CO gases only, i.e., in the furnace hearth and not in the flue. This accounts for the greater coke consumption and its concomitant effects. The increased coke utilization leads to hotter and higher velocity exit gases which carry off approximately 8 per cent of the manganese as stack losses.

On the other hand, the silicate limitation in the ore specification is an attempt to minimize slag losses, since the slag

consists primarily of silicates including manganese silicate. If the basicity of the slag is increased, then the silica can unite with the calcium, magnesium or aluminum, thus allowing the manganese to enter the ferromanganese alloy. A concomitant increase in coke expenses with an increase in the size of the charge burden, however, limits an indefinite increase of basicity via the addition of limestone or some other fluxing agent.

- 
1. "Blast Furnace Gases," Resources for Freedom, Vol. IV, pp. 45-46, Washington, D.C. (1952).
  2. Sully, A. H., Manganese, Butterworth Scientific Publications, London (1955).
  3. Royster, P. H., private communication (1956).
- 

## 2. Electric Furnace

This process is very similar to the blast furnace method except that the heat necessary for the reducing roast is supplied by an electric arc furnace. The ore specifications are identical, but the coke and limestone to ore ratio has been reduced from approximately 2.5-3:1 to 1:3. This, of course, reflects coke's function as a reducing agent only. To be economically competitive with the blast furnace the electric arc furnace must be located near a source of cheap electric power since the production of one ton of ferromanganese consumes 3,000-4,000 kwh and 150-250 pounds of amorphous carbon electrode.

Slag and stack (dust and volatilization) losses are normally in the same range as those from the blast furnace process. However, slag losses increase with the silica content of the ore and reach up to 30 per cent with highly siliceous ores.

- 
1. Sully, A. H., Manganese, Butterworth Scientific Publications, London (1955).

2. Douglas, J. C., private communication (1956).
  3. Vignos, J. C., private communication (1956).
  4. McGonigle, F. A., private communication (1956).
- 

#### B. Silicomanganese

The standard grade silicomanganese contains 65-68 per cent manganese and 18-20 per cent silicon and can be produced via two different techniques. The first process utilizes regular grade manganese ores, quartz, and coke; while the other process simply reduces low grade silicates or silica rich ores or open hearth slag with coke. Present commercial production utilizes the former process, while the latter has not yet been tried on any large scale operation except in Germany in World War I.

In the first process the burden to the electric arc furnace consists of manganese ore, quartz, and coke in the following ratio: 2.7:2.1:1. The quartz assays 96 per cent silica. The energy requirements include approximately 4000 kwh per ton of silicomanganese and also the consumption of 120 pounds of graphite electrode. The carbon and silicon contents in the final product are inversely related and reduction of the carbon content below 1 per cent would necessitate a relatively large increase in silicon content. Total manganese recovery is between 80-85 per cent.

Very few data are available for the process utilizing silicate ores or slags. This situation may be changed in the near future because of the work of the Strategic Materials Corporation.

The work in Germany in 1917-1918 on blast furnace slags containing 10 per cent manganese indicated an increased coke consumption of approximately 20 per cent/ton of silicomanganese as compared to utilizing standard grade manganese ores. Also, both the power input



and electrode consumption were doubled. This is compensated for by the low cost of slag and no expenditure for quartz. The high power costs can easily be attributed to the low manganese content of the slag, which is also responsible for a manganese recovery rate of only 70 per cent. Information about German processes developed and used during World War II has been promised and may become available in the spring of 1957.

A rather significant trend may be in the offing, i.e., the increased demand for a lower grade silicomanganese which analyzes 60-63 per cent manganese and 28-31 per cent silicon. Although it is quite expensive at present, production from silicate ores (rather than regular oxide ores) might significantly decrease the price. Although its future is uncertain, it should not be overlooked from the security viewpoint.

- 
1. Sully, A. H., Manganese, Butterworth Scientific Publications, London (1955).
  2. Foscoe, A., personal communication (1956).
  3. Douglas, J. C., private communication (1956).
  4. Vignos, J. C., private communication (1956).

## SECTION V

### CHARACTERIZATION OF PHYSICAL INPUT COEFFICIENTS AND DOLLAR COST DATA

The processes described in the preceding sections have to be characterized by a number of technical coefficients before they can be considered in a programming model. In this respect, the most important coefficient is that indicating the quantity of mined ore or slag needed to produce the upgraded ore. This coefficient, unique for each process, is determined by the manganese content of the original as well as that of the upgraded ore and the recovery. The same applies to the coefficient that indicates the quantity of upgraded ore of a certain manganese content needed to produce the manganese alloy.

It may be assumed that, once the process has been tried out in the pilot plant, these technical coefficients will not change much in the period under consideration. That is to say that there will not be much difference, at a given scale of production, between the amounts of ore, chemicals, etc. required in 1957 and in 1960, for instance. On the other hand, the effect of changes in the scale of production must not be overlooked.

In addition to these technical coefficients the prices for which the required amounts of ore, chemicals, etc., can be bought will also be required. They make an economic evaluation of the processes possible and are necessary elements in every programming model. It need hardly be said that these prices cannot be assumed to possess the same kind of stability as the technical coefficients. To what extent the final outcome will be affected by variation of future prices will

therefore have to be investigated.

Table 1 shows the information in condensed form for which we are looking:

TABLE I - ILLUSTRATION OF DESIRED INFORMATION

Example: Beneficiation of Aroostook Ores

Type of Ores: Oxides and Carbonates

Process: Nitric Acid (Nossen)

Mn content of mined ore	Recovery				Content x Recovery	Mn content of upgraded ore	NT mined ore per NT upgraded ore
	step 1	step 2	step 3	Total			
0.11				0.80	0.088	0.565	6.420
Feed - 642 NT per day;				Output - 100 NT per day.			
Item	Unit	Needed/NT of mined ore	Price (\$/Unit)	Cost/NT of mined ore	Cost/NT of upgr. ore	Cost/NT of Mn metal	Cost per L.T.U.
Ore	N.T.	1.000	3.929	3.929	25.224	44.645	0.500
Nitric Acid	NT/100	2.181	0.720	1.570	10.080	17.841	0.200
Limestone	NT/100	1.192	0.050	0.060	0.385	0.681	0.008
City Gas	M.cuft	4.219	0.292	1.234	7.922	1.402	0.016
Power	10 kwh	3.068	0.110	0.337	2.164	3.830	0.043
Water	M. gal	1.030	0.050	0.052	0.334	0.591	0.007
Supplies				0.151	0.969	1.715	0.019
				3.404	21.854	38.681	0.433
Labor	MD/100	7.307	0.152	1.111	7.133	12.625	0.141
Overhead				2.929	18.804	33.283	0.373
Operating				11.373	73.015	129.236	1.448
Capital				0.991	6.362	11.261	0.126
Total:				12.364	79.377	140.497	1.574

Source: Report of Senate Hearings dated April 13, 1955, page 109

The information on the other processes, insofar as it is made available to us, has been condensed in similar tables. The latter cannot be shown here since most of them contain privileged information, conveyed

to us for internal use only. We can therefore give here only a verbal characterization of the information that is at the moment in our files.

TABLE 2 - QUALITATIVE SUMMARY OF DATA IN HAND

		Physical Input Coefficients	Dollar Cost Data
	<u>Mining</u>		
A.	<u>Oxide and Carbonate Ores</u>		
	1. Cuyuna Range		
	Strip Mining	bad	poor
	2. Chamberlain Region		
	Strip Mining	bad	poor
	3. Artillery Peak		
	a. Strip Mining	bad	poor
	b. Deep Mining	fair	fair
B.	<u>Silicate Ores</u>		
	Aroostook County		
	a. Strip Mining	bad	bad
	b. Deep Mining	bad	bad
	<u>Beneficiation</u>		
A.	<u>Oxide and Carbonate Ores</u>		
	1. Chemical Processes		
	a. Ammonium Carbamate-Carbonate Leach	good	good
	b. Sulfuric Acid Leach	poor	poor
	c. Nitric Acid Leach	fair	fair
	d. Hydrochloric Acid Leach	bad	bad
	e. Electrolysis	poor	poor
	2. Physical Processes		
	a. Flotation	good	good
	b. Heavy Media Separation	bad	bad
	c. Crushing and Jigging	bad	bad
B.	<u>Silicate Ores and Slags</u>		
	1. Pyrochemical Processes		
	a. Lime Clinkering	poor	poor
	b. Lime Clinkering-Carbamate Leach	fair	fair

<u>Beneficiation (Cont'd)</u>		Physical	Dollar
B.	<u>Silicate Ores and Slags (Cont'd)</u>	Input	Cost
		Coefficients	Data
1.	Pyrochemical Processes (Cont'd)		
c.	Chlorine Vaporization	bad	bad
d.	Chemical Roasting	bad	bad
2.	Pyrometallurgical Processes		
a.	Selective Oxidation of Slag - Spiegel	fair	fair
b.	Electric Furnace Reduction	bad	poor
c.	Selective Oxidation of Pig Iron	bad	fair
3.	Physical Process		
	High Intensity Arc	bad	bad
<u>Alloy Production</u>			
A.	<u>Ferromanganese</u>		
1.	Blast Furnace	fair	fair
2.	Electric Furnace	fair	fair
B.	<u>Silicomanganese</u>	poor	poor

good means in this connection that we are informed about the data for at least three different scales of production so that we can make an approximation of the production function; also, that we have the information in the detail in which we expect to need it.

fair means that we are informed on at most two and often only one scale of production; also, that some details might be missing.

poor means that we are only informed on a few details and have no complete picture of even one scale of production.

bad means almost invariably that we have no useful information at all.

From the table it appears that we are only sufficiently informed on two processes and have detailed information on another six processes (mining included) out of a total of twenty-five processes. Moreover, it should be noted that all figures are estimates of what the actual cost

would be if the process were put in operation at the indicated scales of production. One of the processes on which we feel to be sufficiently informed has already been put in actual operation though on a smaller scale than the one for which we have the estimates. The figures given for the other process (flotation) are based on the experiences the company had in a similar deposit. The other processes for which the information is regarded to be "fair" are, however, not yet beyond the pilot plant stage and, consequently, the basis of the corresponding figures is far less firm.