PN-AAF-781

# PLANT REQUIREMENTS FOR MANUFACTURE OF MANGANESE


DEPARTMENT OF STATE

AGENCY FOR INTERNATIONAL DEVELOPMENT

COMMUNICATIONS RESOURCES DIVISION

Washington 25, D. C.

## FOREWORD

This brochure is one of a series of reports resulting from overseas technical inquiries on factory or commercial establishments, operation, management, and engineering. The report is designed to provide only a general picture of the factors that must be considered in establishing and operating a factory of this type. In most cases, plans for actual installations will require expert engineering and financial advice in order to meet specific local conditions.

Mention of the name of any firm, product, or process in this report is not to be considered a recommendation or an endorsement by the Agency for International Development, but merely a citation that is typical in its field.

This report was prepared in May 1957 by the Wolf Management Engineering Company, Chicago, Illinois, for the industry program through the facilities of the Office of Technical Services, U. S. Department of Commerce.

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Code Number
PR-110

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INTERNATIONAL COOPERATION ADMINISTRATION
OFFICE OF INDUSTRIAL RESOURCES

# TECHNICAL INQUIRY SERVICE

IR-19490 PR

## MANGANESE

### Geology

Manganese is a metallic element which, although widely distributed in nature, never has been found as pure metal. It occurs in combination with other elements, diffused in varying quantities as oxides, silicates, carbonates, sulfides, phosphates, tungstates, columbates, etc. An exception is the metal found alloyed in meteoric iron. Manganese is 16th in the list of the most abundant elements in the earth's crust.

The principal compounds or ores in which managanese is found (it actually is known to be present in 103 compounds), in order of importance are:

| Ore | Description | Chemistry |
|---|---|---|
| Pyrolusite | A black or gray mineral of brilliant metallic lustre, very soft. | Manganese dioxide |
| Braunite | A brownish-black or steel gray mineral, very brittle. | Manganese silicate |
| Hausmannite | A dull brownish-red to black mineral. | Manganese oxide |
| Manganite | A brilliant steel gray or iron black mineral, in orthorhombic crystals or mass. | Hydrous oxide |
| Psilomelane | A smooth iron black or steel gray mineral, in mass or stalactitic form. Very impure. | Hydrous manganese oxide. |

| Ore | Description | Chemistry |
|---|---|---|
| Wad | An amorphous dull brown or black mixture of varying amounts of copper oxides, cobalt oxides, silica. Very soft - sometimes hard by compactness. | Manganese oxide |
| Alabandite | An iron black mineral mass form with cubic cleavage. | Manganese monosulfide |
| Rhodochrosite | A rose pink to red mineral varying to brown, sometimes gray, hexagonal-rhombohedral crystals, sometimes in coarse grained clevable masses. | Manganese carbonate |
| Rhodonite | A pale pink or red mineral - triclinic - massive. | Manganese metasilicate |
| Franklinite | An iron black mineral, slightly magnetic-disseminated crystals, usually octahedral -- sometimes granular aggregates. | Manganese oxide |

The ores often are associated with other metals, particularly with iron oxides and silver ores. Like residual limonite, manganese ore is a secondary product resulting from the removal of more soluble substances during the weathering of slightly manganiferous rock.

Manganese occurs in a wide variety of oxide, silicate and carbonate minerals. The deposits are of four principal geologic types: hydrothermal, sedimentary, residual and metamorphosed. Of these, the sedimentary and residual deposits have been most important economically followed by the metamorphosed. However, any one locality may have evidence of more than one type of deposition.

Hydrothermal ore bodies were formed by deposition from hot water solutions deep within the earth and probably provided the manganese for many high grade ores known today.

Sedimentary deposits, such as those larger deposits in Russia, are layered deposits formed in seas or lakes by either chemical or mechanical action, or both. The chemical actions are results of leaching the manganese minerals from the primary source rocks or other deposits with redeposition as oxides either in place or some distant locality.

Residual deposits result from leaching of gangue minerals of the primary source rock or other deposits, leaving behind a residual concentration of the manganese minerals.

Metamorphosed deposits result from intense alteration by heat and pressure of any of the other types of deposits, but most of the metamorphosed deposits were originally sedimentary.

Presence of the mineral also is recognized in the atmosphere of the sun, in sea water, and in many mineral waters.

## History

The dioxide (pyrolusite) was known to alchemists from early times but was mistaken for magnetic oxide of iron. In 1740 it was found that pyrolusite did not contain iron but that it yielded a definite series of salts.

In 1774 it was discovered that the mineral was a compound of a previously unknown metal and the element then was reduced to its metallic form and given the name "magnesium" from the fact that it was prepared from a compound then known as "magnesia-nigra" (now manganese peroxide or dioxide). In 1808 the name "manganese" was adopted.

The most recent estimate of the world's reserves of manganese ores is one billion tons, of which approximately two-thirds is controlled by the U.S.S.R. and associated countries. The bulk of the remainder is in Africa, India, Brazil, Cuba and the United States.

World mining methods of the ores range from primitive to the most modern of operations; and for the most part mines either are open pits or relatively shallow underground workings. Exceptions occur, such as in some operations in the United States where veins and stringers of rhodochrosite are in quartz and altered granite and are mined to considerable depths.

The largest single manganese mine in the world is the Nsuta mine on the Gold Coast of Africa with a modern open pit of some 3,000 tons per day capacity. The largest single deposit known is the Chiatura in the Caucasus Mountains. All geographical entities, however, have possibilities for increasing reserves by further exploration and discovery.

It will be observed that the U. S. S. R. and India are the major producers of high grade ores and that the total world production approximates 10 million metric tons, bearing a 3-1/2 million ton content of manganese metal.

World Production of Manganese Ore
Per Annum

| | Metric Tons |
|---|---|
| Brazil | 178,700 |
| Chile | 58,400 |
| Cuba | 346,700 |
| Belgian Congo | 509,000 |
| French Morocco | 453,400 |
| Gold Coast | 604,300 |
| India | 1,702,800 |
| Portugese India | 154,500 |
| Japan | 209,000 |
| Turkey | 55,200 |
| South Africa | 649,200 |
| U. S. S. R. | 4,800,000 |
| United States | 285,000 |
| | 10,006,200 |

## Chemistry

To understand manganese and its diversification, both in form and derivitive usage, one should have some fundamental conception of both its mineralogy and chemistry. So that the reader may have some elementary data relative thereto, a short discussion of the chemistry of the mineral follows.

Obviously, in a report such as this, it would be impractical to include all the manganese-bearing ores and their chemical analysis or a complete inorganic and theoretical chemical analysis of its alloys and intermetallic compounds. Such a treatise would, because of its length alone, have to be covered in a separate report. There are several hundred derivitive breakdowns and chemical compositions in use of the oxides, salts, acids, chloride, sulfates, iodides, etc. as well as the biochemical aspects of the mineral.

This report is concerned primarily with the processing of the mineral-bearing ore into material for use as a reagent in steel making (its principal use) and as an ingredient in special alloy steels, with limited mention of its secondary use in the chemical industry and battery manufacturing. These, in reality, are the three principal uses of the world's supply.

At the end of this subject section, a short chemical glossary has been included, listing the principal ores in which manganese is present in appreciable quantities and giving a few of the principal derivitives and their general fields of usage. This will help the reader interpret the subject matter and terminology contained herein.

Manganese, chemically, is a dyad. It has the symbol Mn and an atomic weight of 55 if O = 16 or 54.94 if H = 1. It forms numerous oxides, the best known of which are:

(1) Monoxide, from which the manganous salts may be prepared, is obtained by heating manganese carbonate out of contact with the air.

(2) Sesquioxide, which exists in nature as the mineral braunite, is formed when the monoxide is heated in air to a red heat.

(3) The red or mangano-manganic oxide, which corresponds to the magnetic oxide of iron, does not form salts and exists in nature as the mineral hausmannite.

(4) The black oxide, or dioxide, which occurs in nature as pyrolusite and is used in the preparation of oxygen and chlorine.

(5) The trioxide, which is difficult to prepare and very unstable.

(6) The heptoxide, a heavy, dark red liquid, prepared by treating potassium permanganate with cold concentrated sulfuric acid.

Several of these oxides also occur in a hydrated form, as minerals.

Of the soluble manganous salts, the chief representatives are the sulfate and the chloride. Manganous sulfate is prepared by treating the dioxide with sulfuric acid, simultaneously releasing oxygen. The crystals are used in dyeing and in medicine. The chloride crystals, as a by-product in the manufacture of chlorine by action of hydrochloric acids upon manganese dioxide, are used extensively in calico printing.

Of the insoluble manganese salts, most important are the sulfides and carbonates. The sulfide is obtained when soluble manganous salt is precipitated by alkaline sulfide. The carbonate is a native mineral, rhodochrosite, and is obtained by adding alkaline carbonate to a solution of manganous sulfate or chloride.

Two important classes of manganese compounds are those in which the manganese does not act as a base but as an acid forming element. These are the manganates and permanganates, which may be regarded as the salts of "manganic acid" and "permanganic acid," respectively. The potassium salts of these acids are by far the most important.

Potassium manganate may be prepared by melting manganese dioxide with caustic potash and a little potassium chlorate, dissolving in a small quantity of water and crystallizing by evaporation in a vacuum. Potassium manganate is used in laboratory operations, but it is very unstable, taking up oxygen quickly and depositing hydrated dioxide of manganese.

Potassium permanganate may be obtained by crystallization in the form of purple prismatic crystals. It is a powerful oxidizing agent, extensively used in chemistry, arts and medicine because of the ease with which it parts with oxygen, especially in the presence of organic matter.

## Chemical Glossary

| The Principal Ores | Chemical Symbol |
|---|---|
| Pyrolusite | $MnO_2$ (63.2% av. Mn) |
| Braunite | $Mn_2O_3$-$MnSiO_3$ (69.7% av. Mn) |
| Hausmannite | $Mn_3O_4$ or $2MnO.MnO_2$ (72.5% av. Mn) |
| Manganite | $Mn_2O_3.H_2O$ (62.4% av. Mn) |
| Psilomelane | $MnO_2H_2O$ (45-60% av. Mn) |
| Wad (a mixture of oxides; an impure psilomelane) | 15-40% av. Mn |
| Alabandite | MnS (a manganese monosulfide) |
| Rhodochrosite | $MnCO_3$ (61.7% av. MnO) |
| Rhodonite | $MnSiO_3$ (42% Mn av.) |
| Franklinite | $(FeZnMn)O.(FeMn)_2O_3$ (% Mn av. not calculable) |

## The Principal Oxides, Salts and Acids Formed From Mn*

| Type | Chemical Symbol | Use |
|---|---|---|
| (1) Oxides | | |
| Monoxide | $MnO$ | (Primary) steel industry |
| Sesquioxide | $Mn_2O_3$ | (Secondary) glass, chlorines, electrical batteries and chemical industry. |
| Manganic | $Mn_3O_4$ | |
| Dioxide | $MnO_2$ | |
| Trioxide | $MnO_3$ | |
| Heptoxide | $Mn_2O_7$ | |
| (2) Soluble manganese salts | | |
| Manganous sulfate | $MnSO_4$ | (Secondary) textile, printing, dyeing, and chemical industry. |
| Chlorides | $MnCl_2$ | |
| (3) Insoluble manganese salts | | |
| Sulfides | $MnS$ | (Secondary) paints, varnish, linseed oils. |
| Carbonates | $MnCO_3$ | |
| (4) Acid forming elements | | |
| Manganates | $H_2MnO_4$ | (Secondary) wood preserving, textile bleaching, disinfectants, oxidizing and chemicals. |
| Permanganates | $HMnO_4$ | |
| Potassium manganate | $K_2MnO_4$ | |
| Potassium permanganate | $KMnO_4$ | |

* Chemical and biochemical uses are extensive although not quantity-wise. Actually, less than 10% of the world's manganese production goes to chemical and associated industries. The greatest part goes to steel making. The uses shown in the table are merely representative and not complete. There are many more too numerous to include herein.

## Uses and Characteristics

As previously mentioned, manganese, or manganese ore, has three principal uses:

1. In the steel industry, as a reagent in the steel making process and as an ingredient in special alloy steels.

2. In the chemical industry, as an oxidizing agent in chemical processes and for production of permanganate and other manganese chemicals.

3. In the manufacture of dry cell batteries, as manganese dioxide, the depolarizing agent in the cell.

In addition, although large tonnages are not involved, manganese is important in the production of aluminum and magnesium and is otherwise an important nonferrous alloying element, particularly with copper, for the manufacture of manganese bronzes and high damping alloys.

When used in the production of steel, the manganese ores, for the most part, are first converted for convenience and control to ferromanganese, silico-manganese and spiegeleisen, alloys of manganese and iron of known composition. Manganese is used by the steel industry largely because of its affinity for oxygen and sulfur, its ability to alloy with iron, and its hardening effects.

In the chemical industry, manganese oxide (usually dioxide, $MnO_2$) is a source of oxygen. The manganese ore or metal is used in making various manganese salts.

In the operation of the dry cell battery, hydrogen released from the electrolyte tends to form a nonconductive film around the carbon electrode. Manganese dioxide in the absorbent mix provides free oxygen, which combines with the hydrogen to produce harmless water. Both natural and synthetic $MnO_2$ are used for this purpose, but only certain crystal structures are active.

For uses where manganese is required in exceptionally pure form, such as in the production of stainless steels, certain chemicals, and in the nonferrous metal industries, electrolytic manganese has become increasingly important.

Steel is fundamental to an industrial economy and manganese is essential to steel production. Unless the steel making process is changed from present practice, there is no substitute for manganese. Some substitution

is possible but thus far no processes have been developed to the point where they can be used in quantity.

It is believed also that little substitution can be expected for the battery and major chemical uses. Synthetic battery grade ore is in demand for the manufacture of dry cells, but its cost is too high and production capacities too low for it to be considered for metallurgical purposes.

Approximately 90% of the world's production of manganese-bearing ores goes into the manufacture of steel and alloys. The remainder goes into the chemical and other industries.

Manganese, actually, presents a real problem throughout the world in that as the high grade ores are depleted, industry finds it necessary to lower the grade of ferromanganese produced, while at the same time the steel industry is called upon for increasingly higher grades of steel made to more exacting specifications.

Economics involved in this problem have forced the industry to substitution, beneficiation by certain pyrometallurgical processes which will produce usable manganese from low grade materials, and secondary source recovery measures, all of which are given some consideration in this report.

## The Industry

Like the basic truism previously mentioned that to understand manganese and its diversification one must have some fundamental conceptions of its mineralogy and chemistry, to understand the economics involved one must have knowledge of the industrial format of the industry.

The manganese industry consists of ore producers, traders and ore consumers. The producers are the operators of mines and processing plants. Traders are frequently independent dealers (usually export-import firms) or affiliates of the larger consumers. The consumers are ferro-alloy producers, iron and steel producers, chemical plants, battery manufacturers and segments of the nonferrous metal industry. Industrially, from an operational and economical viewpoint, they are all separate entities and in any analysis their economics must be so treated.

The pattern of this report is concerned with but one of the foregoing, namely, the methods and economics involved in processing the raw manganese-bearing ores, at plant site and as received from the mines, into usable and saleable manganese regardless of its ultimate industry destination or consumer use.

## Economics

In considering the relative economics of manganese extraction, there are many related factors to study. Costs vary with processes, locations, classification of ore, climatic conditions, type and class of labor, transportation facilities, marketing, etc.

There are innumerable processes of extraction, such as flotation and nodulizing, the obtaining of ferromanganese by blast furnace smelting, the producing of manganese ferroalloys by an electric furnace process and electrolytic manganese by the electrolytic process. Electrolytic manganese is an almost pure metal and, although it has limited factors of tonnage and costs, does have an advantage in that low-grade ores can be used for feed, despite higher costs.

It is not the intention to illustrate herein the variable processes by which manganese is extracted or to furnish a metallurgical, chemical, biochemical or synthetic treatise on the subject, for, as previously mentioned, to do so would require a lengthy and separate document.

Processing, regardless of the method employed, is highly complex and involved. To illustrate this fact, it seems advisable to present a short and concise dissertation on the cyclic methods of electrolytic production of hydrometallurgical reagents for the processing of manganese ores, or what is frequently referred to as the sodium sulfate process. It is shown to illustrate one method of manganese extraction, the flow method required, and the results obtained.

### Sodium Sulfate Process*

In the cyclic method of processing manganese ores using sodium sulfate as the basic reagent, the sodium sulfate is electrolyzed in a diaphragm cell to give an anolyte-containing sulfuric acid and an catholyte-containing caustic soda, a part of which is carbonated in a cyclic manner to form soda ash.

The reduced ore is leached with the anolyte to dissolve the manganese, and the impurities are precipitated by addition of catholyte. Manganese in the pregnant solution is precipitated as synthetic rhodochrosite with a carbonated catholyte, and sodium sulfate is regenerated. Calcining the manganese carbonate gives a high grade product, and carbon dioxide is returned to the carbonated step.

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* An article by J. Bruce Clemmer, Carl Rampacek and P. E. Churchward, Journal of Metals, Jan. 1955, published by American Institute of Mining and Metallurgical Engineers, Inc., 29 West 39th Street, New York 18.

The results of laboratory tests, using cells equipped with synthetic fiber diaphragms and permselective membranes which permit transfer of anions or cations during electrolysis, are described in the following:

## Cyclic Processing of Reduced Ore

| Roasting | Total | Acid Soluble |
|---|---|---|
| Ore roasted 4 min. at 900°C. with natural gas - reduced ore assay, percent Mn | 15.35 | 14.25 |

**Leaching**

| | |
|---|---|
| Total weight of ore leached, g. | 11,500. |
| Average extraction, percent of total Mn | 88.8 |
| Average extraction, percent of acid-soluble Mn | 95.7 |
| Acid used (43,320 m/anolyte containing 83.5 g. per liter $H_2SO_4$), g. | 3,534. |
| Weight of Mn leached, g. | 1,568. |
| $H_2SO_4$ per lb. Mn leached, lb. | 2.25 |
| Weight of Mn recovered, g. | 1,517. |
| $H_2SO_4$ per lb. Mn recovered, lb. | 2.33 |

**Purification of Leach Liquor**

| | |
|---|---|
| $H_2O_2$ used, g. | 42.3 |
| $H_2O_2$ per lb. Mn recovered, lb. | 0.028 |
| NaOH used (4,526 m/catholyte, 66.99 NaOH per liter), g. | 303. |
| NaOH per lb. Mn recovered, lb. | 0.2 |

**Pregnant Liquor Assay**

G Per Liter

| | Mn | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | $H_2SO_1$ | pH |
|---|---|---|---|---|---|---|---|
| Before purification | 37.9 | 3.29 | 1.47 | 2.69 | 0.3 | 3.2 | 2.0 |
| After purification | 34.6 | 0.09 | 0.29 | 0.26 | 0.3 | -- | 5.5 |

**Precipitation**

| | |
|---|---|
| Carbonated catholyte used, equivalent to NaOHg | 2,185. |
| NaOH per lb. Mn recovered, lb. | 1.55 |

## Final pH Establishment

| | |
|---|---|
| Catholyte equivalent to NaOHg | 235. |
| NaOH per lb. Mn recovered, lb. | 0.17 |

## $MnCO_3$ Product

| | Assay, Percent | | | | | | |
|---|---|---|---|---|---|---|---|
| | Mn | $SiO_2$ | $Al_2O_3$ | S | CaO | MgO | P |
| Dried at 110°C. | 47.8 | 0.28 | 0.02 | 0.54 | 1.25 | 0.37 | <0.01 |
| Ignited at 850°C. | 64.5 | 0.33 | 0.03 | 0.73 | 1.70 | 0.5 | <0.01 |

Recovery of acid-soluble Mn in ore, percent 92.6

## Regenerated $NaSO_4$

| | Analysis G Per Liter | | | | | | |
|---|---|---|---|---|---|---|---|
| | Mn | $SiO_2$ | $R_2O_3$ | MgO | Cl | S | Specific Gravity |
| First cycle | 0.008 | 0.010 | 0.030 | Trace | 0.016 | 44.65 | 1.162 |
| Fourth cycle | 0.006 | 0.015 | 0.015 | Trace | 0.025 | 44.50 | 1.165 |

## Reagent and Power Requirements Per Lb. Mn Recovered

Reagents made by electrolysis:

| | |
|---|---|
| NaOh, lb. | 1.92 |
| $H_2SO_4$, lb. | 2.33 |
| Power required (total) kw.-hr. | 3.9 |

Other reagents:

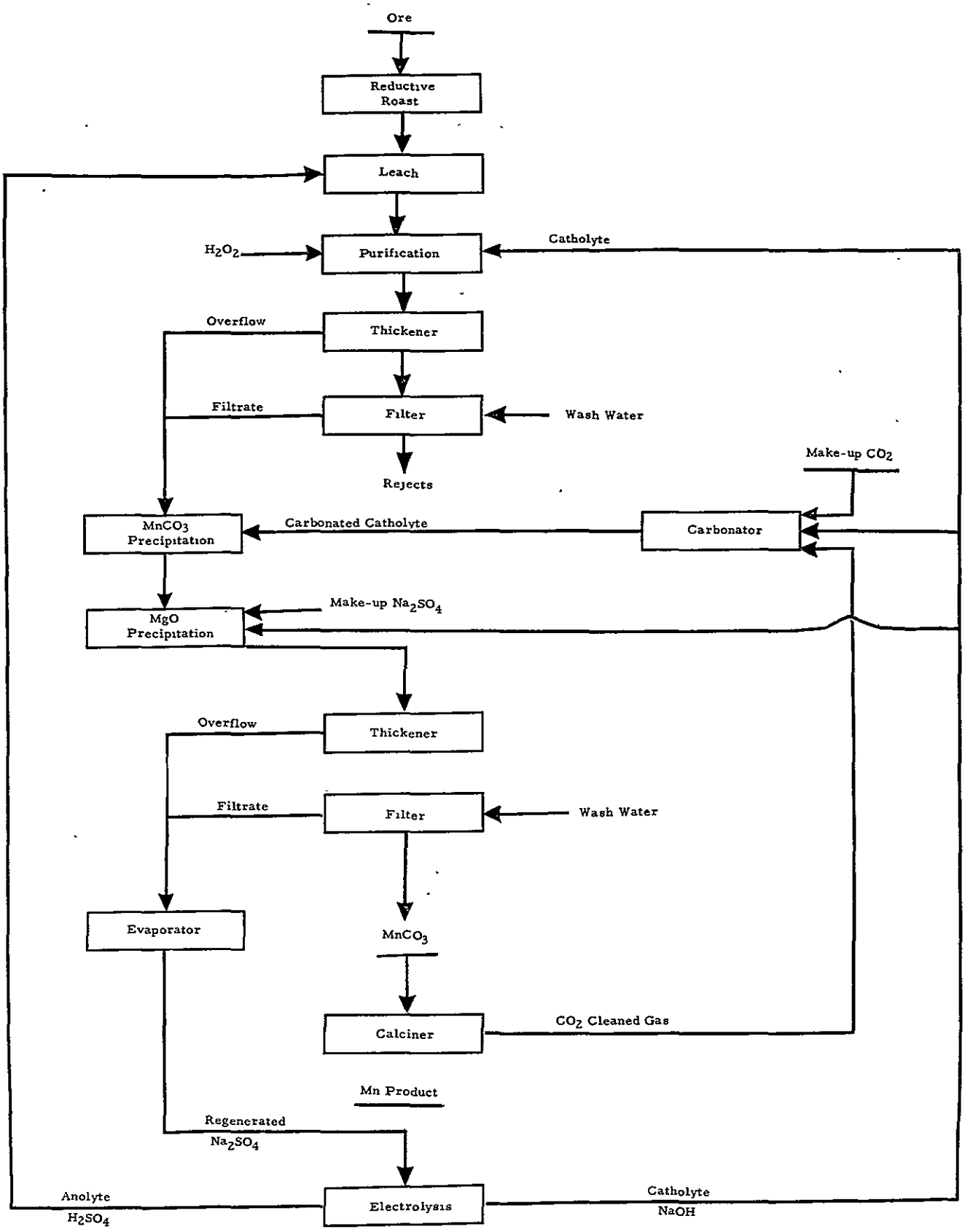
| | |
|---|---|
| $H_2O_2$, lb. | 0.028 |
| $Na_2SO_4$ (make-up), lb. | 0.2 |
| $CO_2$ (make-up), lb. | Not determined |

Thickening, Filtering, and Washing

| | Area Sq. Ft. Per Ton Dry Solids Per Day | Lb. Per Lb. of Dry Solids | Percent Solids | |
|---|---|---|---|---|
| | | | Feed | Under Flow |
| **Residue** | | | | |
| Thickening (no flocculent) | 10.9 | | 18.3 | 40.8 |
| Filtration and washing | 1.25 | | 40.8 | 65.0 |
| Wash water | - | 1.5 | - | - |
| **Precipitate** | | | | |
| Thickening (no flocculent) | 13.5 | - | 3.7 | 35.5 |
| Filtration and washing | 0.75 | - | 35.0 | 54.0 |
| Wash water | - | 2.0 | - | - |

Flow Sheet for Processing Manganese Ores

by the Sodium Sulfate Process




Source: Article by J. Bruce Clemmer, Carl Rampacek and P. E. Churchward, Journal of Metals, Jan. 1955, published by American Institute of Mining and Metallurgical Engineers, Inc., 29 West 39th Street, New York.

## Process

This report, however, is primarily concerned with a single process that would be most applicable to the average economic situation and location and most universally acceptable for consideration by a prospective investor. The electrolytic process, therefore, is presented as one of the acceptable types designed to give satisfactory production of the end product with reasonable assurance of a successful operation.

Anyone, however, contemplating a major investment in as complex an industry as the treating and extraction of manganese ore, where related factors have a decided influence on the outcome, is cautioned to secure the services and advice of a reputable firm of consulting management engineers who would prepare a complete administrative, operative and financial analysis commensurate with local conditions and process involved, before a manganese production enterprise is begun.

The electrolytic manganese process consists of several essential steps. These may vary somewhat in nature, in accordance with the ore being treated, the availability of various types of fuel and other local factors. These steps are:

1. Preparation of the ore for leaching, ordinarily by a reducing roast.

2. Leaching the ore or calcine.

3. Purification of the solution, including sulfide purification and regulation of reducible sulfur compounds.

4. Electrolysis of the solution, including selection and preparation of anode and cathode, control of pH, current density and temperature, cell structure, and diaphragms.

5. Stripping of product.

### Preparation of Ore for Leaching

The mine run ore is passed through a grizzly, or screen, into the coarse ore bin from which it is conveyed to the primary crusher and thence to the secondary screen and crusher. After these crushing operations, the material is conveyed into a steel storage bin. (See Figures 1, 2, 3 and 4.)

From this supply the material is batched by weight, and the batches are fed into the thermo ball or rod mill (See Figure 5), which is equipped with an air classifier. Preheated air entering the classifier dries the ground ore and removes it from the ball or rod mill.

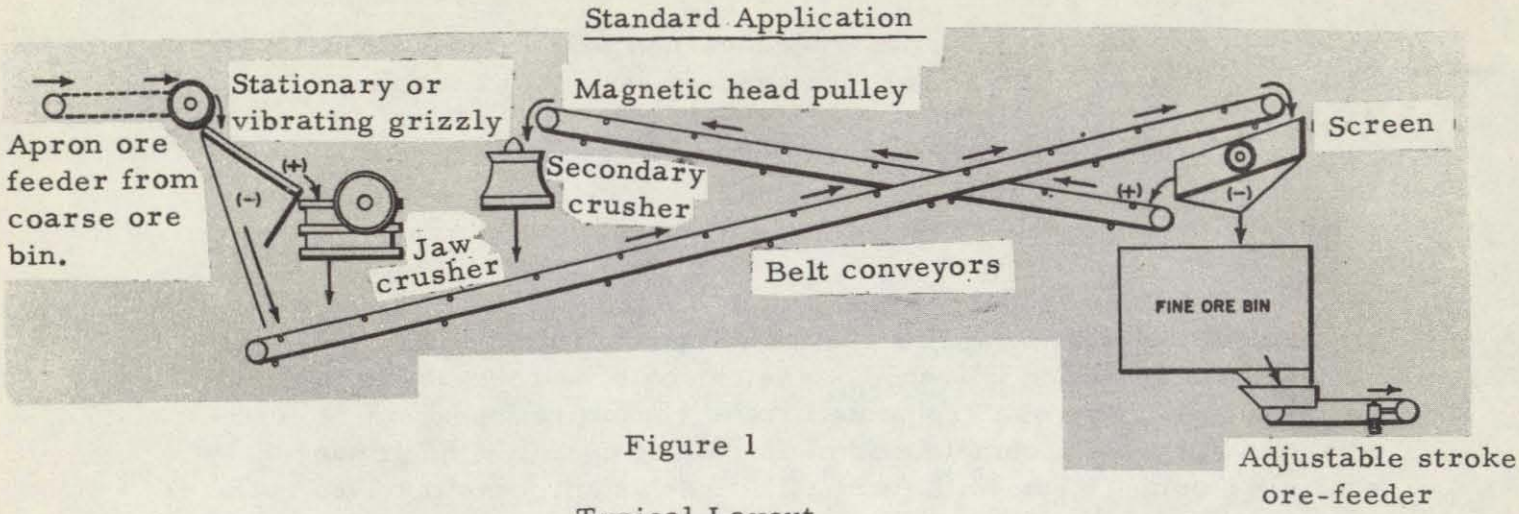



Figure 1

Typical Layout

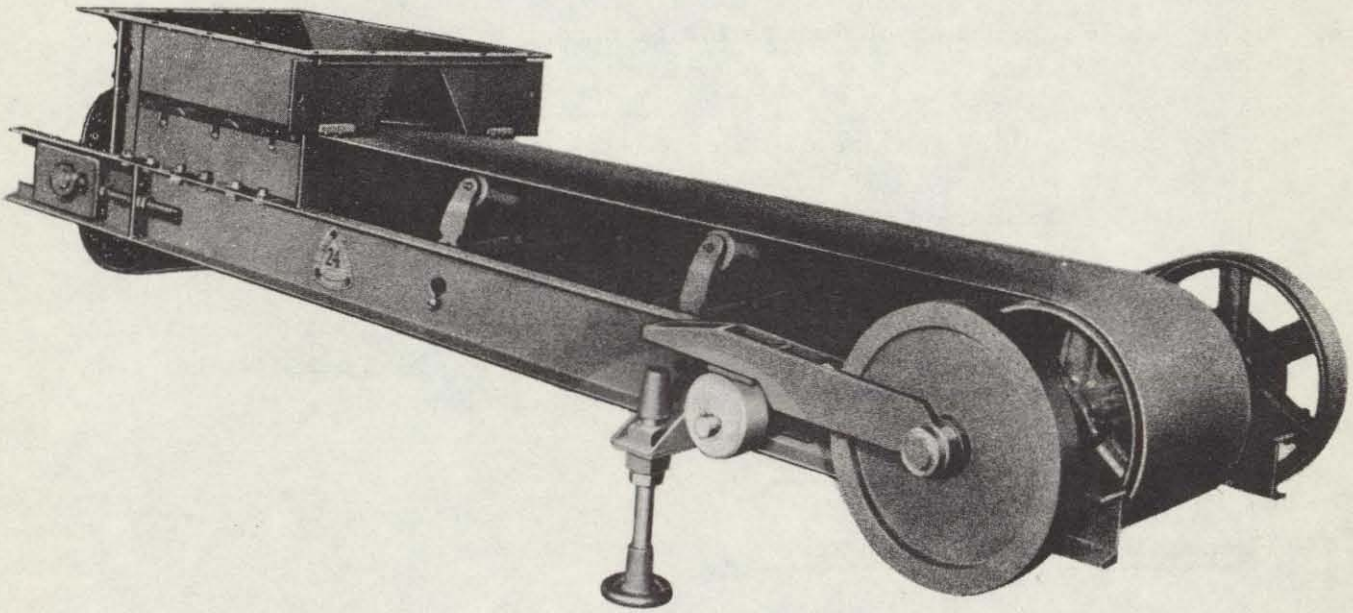


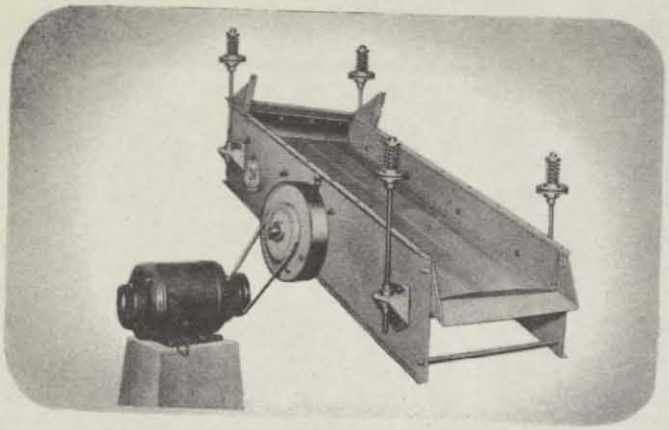
Figure 2

Typical Ore Feeder



Courtesy Denver Equipment Co.
Denver, Colorado

SINGLE DECK SCREEN



DOUBLE DECK SCREEN

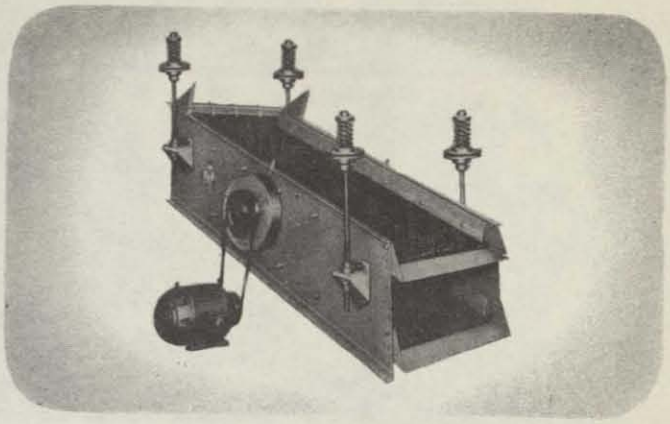


Figure 3

Typical Ore Screens or Grizzlies
(Stationary, vibrating and multiple-level types are used, depending on type of installation.)

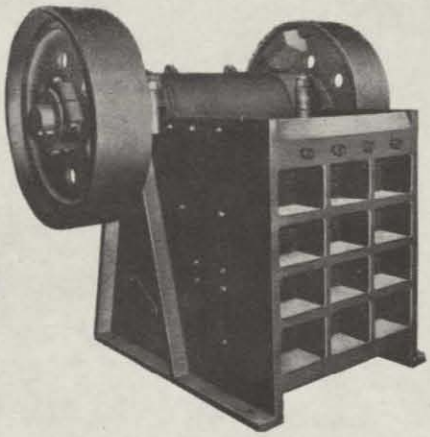


Figure 4

Typical Jaw Crusher
(Secondary crushers are of lighter construction.)



Courtesy Denver Equipment Co.
Denver, Colorado

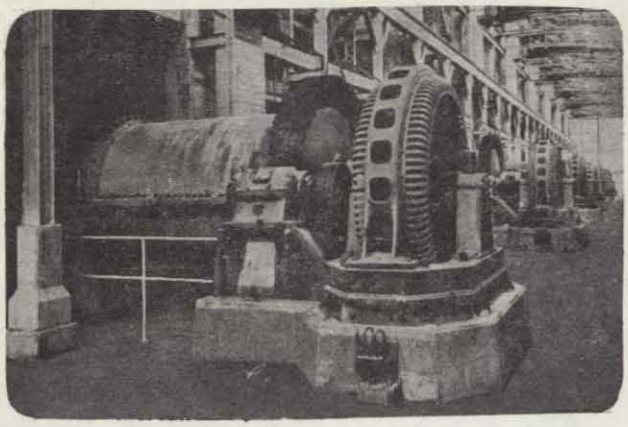


Figure 5

Typical Ball Mill

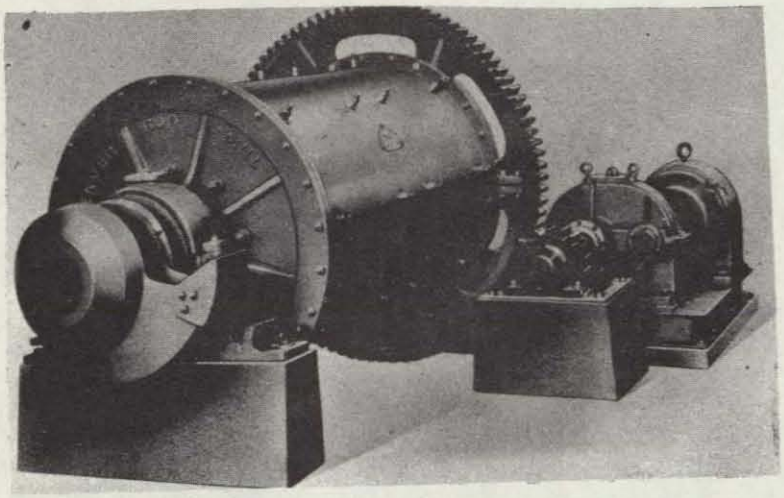


Figure 6

Typical Rod Mill



Courtesy Denver Equipment Co.
Denver, Colorado

The cyclone dust collector collects the ground product and drops it into another steel storage bin from which it is fed to the Skinner type furnace. Gas, oil and solid fuel have been used successfully for reducing manganese ore for the preparation of electrolyte.

From the furnace, the material is cooled by passing through a cooler and then into steel storage tanks. From this source, the crushed ore is fed to the leach tanks.

## Leaching the Ore or Calcine

The leaching step is the simplest and most standardized of the process steps. The leach tanks are equipped with stainless steel ship-type agitators (See Figure 7), and the capacity may range from 3,400 to 8,000 gallons.

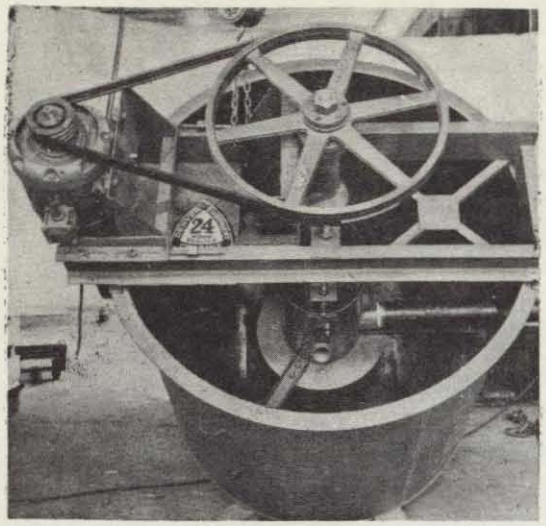
After the calcine is charged into the leach tank, sulfuric acid is added to keep the pH at 2.5, the finish point of the leach. Ammonium sulfate is added to maintain a concentration of 135-140 grams per liter. Time of leach is approximately 1-1/4 to 1-1/2 hours.

After the leach is finished at 2.5 pH, it is neutralized by adding ammonia, or calcine, to pH 6.5. When the leach is neutralized, iron and aluminum hydroxides are precipitated and carried down with molybdenum, arsenic and silica. The leach then is pumped to the thickeners and the overflow sent to the purification step. Neutralization of the leach solution with ammonia gives better settling than neutralization with calcine.

## Purification of the Solution

The leach solution at pH 6.5 flows to a stainless steel Flomix, and hydrogen sulfide is added in the solution line. The Flomix is a totally enclosed double agitator. In this process, the copper, zinc, and most of the nickel and cobalt are precipitated.

After filtration, the solution is further purified by adding ferrous sulfate and oxidizing to precipitate ferric hydroxide. The solution is now free from metallic impurities as well as practically all sulfur compounds. The presence of magnesium is without adverse effect on the electrolysis but will eventually separate, coating the cooling coils and diaphragms. The separation of the magnesium salt in the cell is avoided by chilling the solution to 10-13°C. in a suitable apparatus and collecting the salts separated in this way.



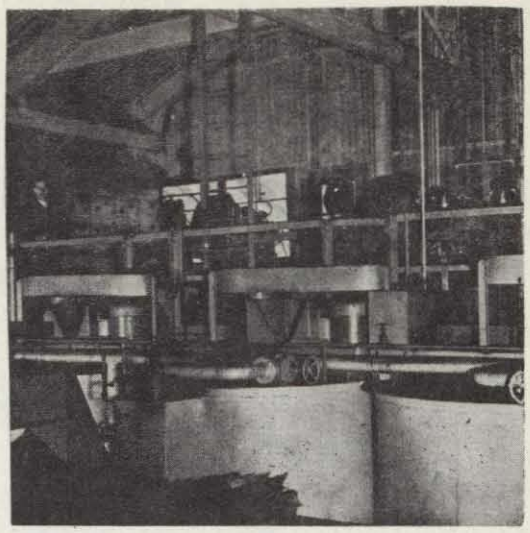


Figure 7

Typical Agitators

Courtesy Denver Equipment Co.
Denver, Colorado

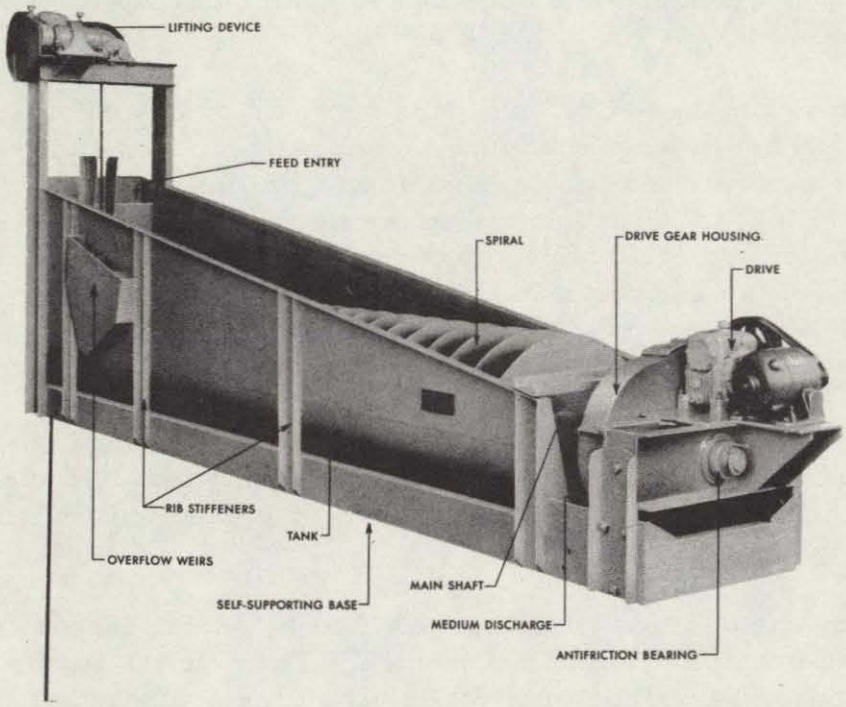



Figure 8

Typical Densifier

Courtesy Western Machinery Company
San Francisco, California

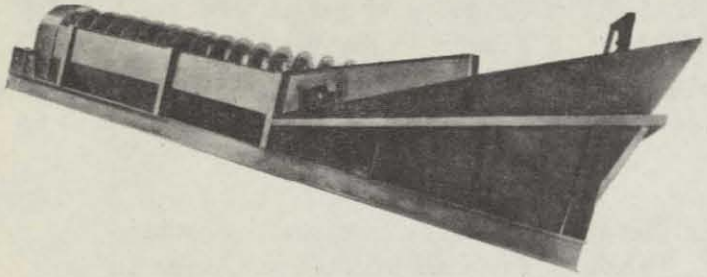


Figure 9

Typical Spiral Dewaterer

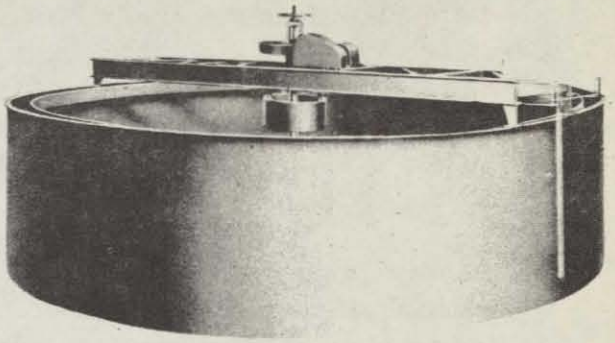


Figure 10

Typical Thickener

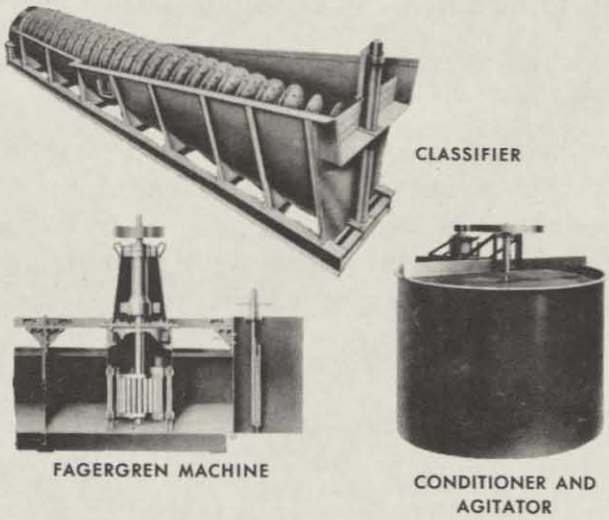



Figure 11

Typical Equipment



Courtesy Western Machinery Co.
San Francisco, California

## Electrolysis of the Solution

The deposition of manganese is carried out in a diaphragm cell. The electrolyte is fed into the cathode compartment and passes through the diaphragm into the anode compartment. The optimum concentration of salts in the solution actually surrounding the cathode is about 12 grams per liter of manganese as sulfate, and 130-136 grams ammonium sulfate. Ammonium sulfate added to the manganese electrolyte prevents precipitation of manganese as the pH increases in the catholyte and increases the conductivity of the solution.

General experience shows that the best temperature for practical electrowinning of manganese is about 35°C. Although the cell voltage drops with increasing temperature, the drop in current efficiency more than offsets this so that no advantage in power consumption per pound of manganese deposited is obtained.

The desired temperature in the cells is obtained by inserting lead coils through which a cooling solution is circulated. Current density and time of deposition can be varied over a wide range with only slight variation in current efficiency, provided proper cell temperature is maintained.

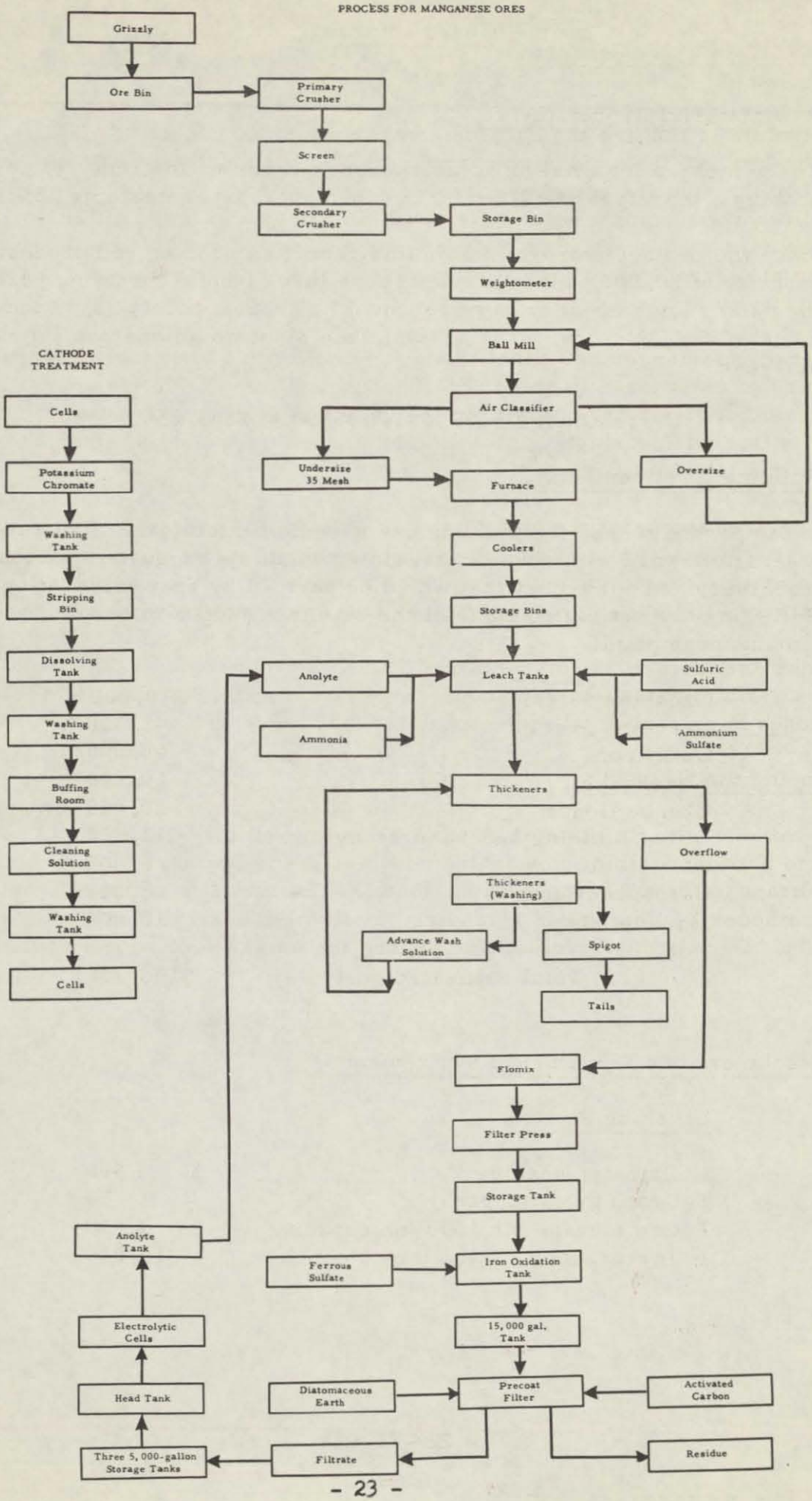
Anodes are of various compositions. Lead-tin-cobalt, lead-antimony-tin with cobalt, and lead-silver anodes have been used. Stainless steel cathodes have proven to be the most satisfactory.

## Stripping the Product

The cathode with its plate of manganese is dipped in 1% dichromate solution to prevent staining in washing with water and drying. This is highly important to the appearance of the metal. The metal is stripped from the cathodes by flexing and removing any tightly adhering metal with a mallet. Canvas diaphragms have proven the most effective and economical.

FLOW SHEET OF ELECTROLYTIC

PROCESS FOR MANGANESE ORES



## Cost Factors

### Raw Material Requirements

The content of manganese in the raw ore covers a wide range of percentages; therefore, this report is based on an ore containing 25% Mn.

Since the projected operations in this report call for an end product capacity of 20,000 pounds of manganese in a 24-hour operating period, the daily requirement of raw ore would be approximately 35.33 tons at a cost of $100 per ton. It is assumed the plant would operate 250 days per year.

Calculation: $35.33 \times \$100 \times 250 = \$883,250.$

### Building Requirements

In temperate zones, the building costs would be nominal. Structural steel framework with sheet metal siding would be adequate for housing machinery and equipment that would be harmed by open installation. Following are estimated costs of the buildings judged to be adequate for a manganese plant:

| | |
|---|---|
| Crushing Section | $10,000 |
| Leaching Section | 42,200 |
| Cell Room | 60,000 |
| Warehouse | 10,000 |
| Change House | 10,000 |
| Office Building and Laboratory | 12,500 |
| Electrical Shop | 6,000 |
| Carpenter Shop | 6,000 |
| Machine Shop | 10,000 |
| Total estimated cost | $166,700 |

### Machinery and Equipment Requirements

#### Crushing Section

| | |
|---|---|
| 1 Grizzly, shaking | $ 500 |
| 1 Grate grizzly, bar | 50 |
| 1 Ore storage bin, 500 ton capacity | 5,000 |
| 1 Jaw crusher, 21-inch by 36-inch. | 15,000 |

Crushing Section (Cont'd)

| | | |
|---|---|---|
| 1 | Gyratory crusher, 40 hp. motor | $13,000 |
| 1 | Symons tyrod screen | 750 |
| 1 | Belt conveyor, 18 inches wide | 3,400 |
| 3 | Sly dust-collector units | 48,100 |
| 1 | Hardinge thermo mill, 10 by 36 inches, with 300 hp. motor | 45,000 |
| 1 | Scrubbing tower | 750 |
| 1 | Ore storage bin, 50-ton | 400 |
| 1 | Oil meter | 150 |
| | Total | $132,100 |

Roasting Section

| | | |
|---|---|---|
| 1 | Screw conveyor, 10 hp. motor | $ 750 |
| 1 | Weightometer | 2,000 |
| 1 | Skinner furnace, 16-ft. diameter | 48,400 |
| 1 | Baker cooler, 7 by 20 ft., 10 hp. motor | 5,000 |
| 1 | Temperature recorder | 750 |
| 1 | Redler conveyor #1 | 5,000 |
| 1 | Calcine storage bin, 16 by 20 ft. | 500 |
| 2 | Rotary feed gates | 900 |
| 1 | Vibrator | 125 |
| 1 | Draft gages | 500 |
| | Total | $63,925 |

Leaching Purification Section

| | | |
|---|---|---|
| 2 | Lead and brick-lined tanks, 16-ft. diameter | $4,335 |
| 6 | Valves | 264 |
| 2 | Turbine agitators, 60-inch | 4,335 |
| 1 | Packless pump | 1,500 |
| 1 | pH meter | 200 |
| 1 | Redler conveyor #2 | 4,000 |
| | Total | $14,634 |

Thickener Section

| | | |
|---|---|---|
| 2 | Thickeners, 75 by 10 ft. | $ 20,000 |
| 4 | Thickeners, 50 by 10 ft. | 32,000 |
| | Lead for thickener liners | 22,000 |
| 6 | Diaphragm valves | 792 |

Thickener Section (Cont'd)

| | | |
|---|---|---|
| 6 | Diaphragm pumps | $ 4,200 |
| 5 | Agitator tanks | 300 |
| 3 | Portable mixers | 1,200 |
| 1 | Stainless steel screen | 100 |
| 1 | Water meter | 50 |
| | Tailing line | 750 |
| 1 | Tailing pump | 800 |
| | Asphalt pad under thickeners | 5,000 |
| | Total | $ 87,192 |

Hydrogen Sulfide Purification Section

| | | |
|---|---|---|
| 1 | Turbo absorber, 24-inch | $ 1,300 |
| 1 | Tank, 2,600-gallon | 430 |
| 1 | Diaphragm valve, 2-inch | 25 |
| 4 | Stainless steel valves, 6-inch | 1,000 |
| 1 | Header, 500-lb. pressure | 100 |
| 1 | Pressure reducer | 100 |
| 1 | Automatic $H_2S$ regulator | 500 |
| 1 | #13 rotameter and recorder | 1,500 |
| | Total | $ 4,955 |

Filtration Section

| | | |
|---|---|---|
| 1 | Shriver filter press, 42 by 42 inches | $18,000 |
| 2 | #3 Shriver diaphragm pumps | 2,000 |
| 2 | Nitrate storage tanks, 70 by 8 ft. | 20,000 |
| | Lead for tank linings | 9,000 |
| 2 | Diaphragm valves, 6-inch | 500 |
| 2 | Diaphragm valves, 2-inch | 50 |
| 2 | Pulping tanks, 5 by 5 ft. | 150 |
| 2 | Portable mixers | 500 |
| 1 | Electric hoist, 1-ton capacity | 325 |
| | Total | $ 50,525 |

Iron Purification Section

| | | |
|---|---|---|
| 3 | Agitator tanks, 11 by 10 ft. | $ 900 |
| 3 | Turbo-absorbers, 24-inch | 3,000 |
| | Lead for tanks | 5,500 |
| 3 | Motors, 10 hp. | 1,050 |

Iron Purification Section (Cont'd)

| | | |
|---|---|---|
| 3 | Sparger rings | $ 100 |
| 1 | Diaphragm valve, 6-inch | 250 |
| 1 | #13 rotameter and recorder | 1,500 |
| 1 | Packless pump, 8 by 6 inches, 10 hp. | 1,500 |
| 1 | Dry reagent feeder | 100 |
| 1 | Aging tank | 10,000 |
| 1 | Diaphragm valve | 250 |
| 1 | pH meter | 200 |
| 1 | Diaphragm valve, 2-inch | 100 |
| | Total | $ 24,450 |

Magnesium Removal Section

| | | |
|---|---|---|
| 1 | Agitator tank, 16 by 10 ft. | $ 800 |
| | Lead for lining tank | 650 |
| | 2-inch lead pipe for coils, 1,635 ft. | 1,308 |
| 1 | Turbine mixer, 20 hp. | 2,166 |
| 1 | Diaphragm valve, 2-inch | 25 |
| 1 | Water pump, 2-inch | 200 |
| 1 | Cooling tower, 30 by 31 ft. | 8,302 |
| 1 | Bird centrifuge, 36-inch | 15,000 |
| 1 | Packless pump, 2-inch | 700 |
| | Total | $ 29,151 |

Electrolytic Cell Room Section

| | | |
|---|---|---|
| 1 | Cathode storage tank, 10,500 gallon | $ 400 |
| 1 | Iron aging tank | 400 |
| 1 | Purification storage tank, 15 by 8 ft. | 400 |
| 3 | Diaphragm valves, 3-inch | 150 |
| 3 | Diaphragm valves, 2-inch | 75 |
| 1 | Agitator tank, 10 by 10 ft. | 300 |
| 1 | Agitator, 5 hp. motor | 800 |
| 1 | Diaphragm valve, 3-inch | 50 |
| | Lead for lining tanks | 1,600 |
| 1,463 | Anodes | 13,167 |
| 2,238 | Cathodes | 26,968 |
| 66 | Cells | 17,160 |
| | Asphalt floor | 2,500 |
| 1,680 | Cathode frames | 9,744 |

Electrolytic Cell Room Section (Cont'd)

| | | |
|---|---|---|
| 1,760 | Anode frames | $ 5,280 |
| 1,680 | Cell spacer blocks | 672 |
| | Copper bus bar | 7,056 |
| | Lead pipe and sheet | 3,500 |
| | Iron pipe and valves | 2,500 |
| | Rubber-lined valves | 1,500 |
| 2 | Water pumps, 8-inch | 2,000 |
| 1 | Acid proof pump, 2-inch | 400 |
| 1 | Buffer | 5,000 |
| 8 | Hoists | 5,000 |
| 1 | Manganese storage bin | 500 |
| | Wash tanks | 4,000 |
| | Floor trucks | 2,500 |
| | Racks for electrodes | 250 |
| | Control laboratory equipment | 23,000 |
| | Assorted tools | 2,500 |
| | Miscellaneous items | 6,000 |
| 2 | pH meters | 400 |
| 1,380 | Cathode clips | 1,035 |
| | Copper bus bar | 450 |
| | Cooling tower | 19,085 |
| 1 | Generator | 15,000 |
| | Total | $181,342 |

Miscellaneous Equipment

| | | |
|---|---|---|
| 1 | #13 rotameter and recorder | $ 1,500 |
| 1 | Centrifugal pump | 1,300 |
| 1 | Storage tank, 231,000-gallon | 10,000 |
| 5 | Diaphragm valves, 3-inch | 250 |
| 1 | Diaphragm valve, 2-inch | 25 |
| | Hose line, 6 outlets or launder | 750 |
| 1 | Acid storage tank, 92.5 ton for $H_2SO_4$ | 500 |
| 7 | Cast iron valves | 175 |
| 1 | Acid meter | 125 |
| 1 | Air compressor | 1,200 |
| 1 | Oil storage tank | 800 |
| | Lead lining for tanks | 4,500 |
| | Lead pipe | 10,000 |
| | Miscellaneous items | 2,000 |
| | Laboratory, carpenter, electrical and machine shop equipment | 42,000 |
| | Automobiles and trucks | 18,000 |
| | Ammonia tank truck | 10,000 |
| | Total | $103,125 |

| | |
|---|---|
| Total equipment expenditure | $691,399 |
| Rectifier | $ 150,000 |
| Substation | 60,000 |
| | $ 210,000 |
| Estimated installation cost, including concrete floors, piers and foundations (Some machinery prices include installation.) | $ 47,260 |
| Engineering | $ 40,000 |

Chemicals Required to Start Plant

| | | |
|---|---|---|
| Ammonium sulfate | 465 tons | $ 21,948 |
| Sulfuric acid | 241 tons | 3,880 |
| Hydrogen sulfide | 688 lbs. | 221 |
| Ferrous sulfate | 4,958 lbs. | 139 |
| Filter aid | 1,377 lbs. | 38 |
| Ammonia | 10,328 lbs. | 619 |
| Filter cloth | 127 sq. yds. | 76 |
| Total | | $ 26,921 |

Total Cost of the Plant (Estimated)

| | |
|---|---|
| Buildings | $ 166,700 |
| Machinery | 691,399 |
| Rectifier | 150,000 |
| Substation | 60,000 |
| Installation | 47,260 |
| Freight and cartage | 22,000 |
| Engineering | 40,000 |
| Total | $1,177,359 |

The production of 20,000 pounds of manganese per day would require the operation of 64 cells for a 24-hour operating period, as each cell has a daily capacity of 312 pounds every 24 hours.

## Annual Costs

| Direct Labor | Three-Shift Labor Cost |
|---|---|
| Crushing Section (12 men per shift) 36 men @ $1.25 per hour | $ 90,000 |
| Roasting Section (6 men per shift) 18 men @ $1.25 per hour | 45,000 |
| Leaching and Purification Section (9 men per shift) 27 men @ $1.25 per hour | 67,500 |
| Electrolysis Section (10 men per shift) 30 men @ $1.25 per hour | 75,000 |
| Trucking, Warehouse and Packaging Section (10 men per shift) 30 men @ $1.25 | 75,000 |
| Total direct labor per year | $352,500 |

| Indirect Labor | |
|---|---|
| Maintenance Section (4 men per shift) 12 men @ $2.00 per hour | $ 48,000 |
| Supervision (4 men per shift) 12 men @ $2.25 | 54,000 |
| General Superintendent (per year) | 6,000 |
| General Manager (per year) | 10,000 |
| Stenographic and Office Force (6 men for 1 shift) 6 men @ $1.50 | 18,000 |
| Total indirect labor per year | $136,000 |

Selling and General Expense (Per Year)

| | |
|---|---|
| Research and development | $ 10,752 |
| Electricity | 19,538 |
| Chemicals | 46,997 |
| Selling expense | 20,000 |
| Total per year | $ 97,287 |

Sales Revenue

Based on a daily production of 10 tons of manganese:

20,000 lbs. × 250 days = 5,000,000 lbs. per year.

5,000,000 lbs. @ $0.35 = $1,750,000.

Total sales revenue per year = $1,750,000.

Estimated Working Capital

| | |
|---|---|
| Raw ore (50-day supply) | $ 168,650 |
| Chemicals (necessary to start operation) | 26,921 |
| Direct labor (50-day period) | 70,500 |
| Indirect labor (2-month period) | 27,200 |
| Selling, general and administrative expense (2-month period) | 9,548 |
| Total | $ 302,819 |

Estimated Fixed Capital

| | |
|---|---|
| Land | - - |
| Buildings | $ 166,700 |
| Machinery | 691,399 |
| Rectifier and substation | 210,000 |
| Installation and engineering | 87,260 |
| Total | $1,155,359 |

## Estimated Total Capital

| | |
|---|---|
| Working capital | $ 302,819 |
| Fixed capital | 1,155,359 |
| Total | $ 1,458,178 |

## Profit and Loss Projection

The following is an estimated profit and loss statement for a one-year period of operation:

| | | |
|---|---|---|
| Net sales | | $ 1,750,000 |
| Less cost of goods sold: | | |
| Raw material | $ 883,250 | |
| Direct labor | 352,500 | |
| Indirect labor | 136,000 | 1,371,750 |
| Gross profit on sales | | 378,250 |
| Depreciation: | | |
| Buildings (5%) | 8,335 | |
| Substation (5%) | 3,000 | |
| Machinery (10%) | 69,140 | |
| Rectifier (10%) | 15,000 | |
| Total depreciation | 95,475 | |
| Engineering, installation, freight and cartage expense | 10,926 | |
| Selling and general expense | 97,287 | 203,688 |
| Net profit (before taxes, insurance and miscellaneous expense) | | $ 174,562 |

## Manganese Consultants

Denver Equipment Company, Denver, Colorado
Traylor Engineering and Manufacturing Company, Allentown, Pennsylvania
Allis-Chalmers Manufacturing Company, Chicago, Illinois
Hardinge Company, Inc., York, Pennsylvania
Fairbanks-Morse & Company, Chicago, Illinois
The Mine and Smelter Supply Company, Denver, Colorado
Western Machinery Company, San Francisco, California
Wolf Management Engineering Company, Chicago, Illinois

## TECHNICAL INQUIRY SERVICE REPORTS

Information relating to establishment of a manufacturing plant has been furnished by the Technical Inquiry Service in the following reports:

### CHEMICAL AND RELATED PRODUCTS

Fermentation Ethyl Alcohol
Furfural
Laundry and Milled Toilet Soap
Pharmaceutical Products
Potash
Salicylic Acid
Small Fertilizer Plant
Sulphuric Acid
Vinyl Floor Tiles

### FOOD PROCESSING

Candy and Confectionary
Carob Molasses
Crude Olive Oil
Dehydrated Molasses
Fish Meal
Fish and Shrimp Processing
Ice Cream
Molasses
Orange Juice
Rice
Rice Bran Oil
Salted Peanuts
Slaughtering and Meat Packing Plant
Soybean Processing
Starch
Unfermented Grape Juice
Wheat Flour
Wheat Milling

NOTE: Additional plant requirements data have also been published in longer plant operations and plant requirements reports, for industries listed in the Technical Aids Branch "Industrial Reports and Publications" bulletins.

METALS

Aluminum Architectural Specialties
Bicycles
Coil Springs
Copper Tubing
Copper Wire - Drawing and Insulating
Fluorescent Lamp Ballast
Fractional and Small Horsepower Electric Motors and Direct Starters for Squirrel-Cage Motors
Galvanized Steel Pipe
Latch Needles
Manganese
Metal Spinning
Mineral Wool
Ornamental Ironwork
Porcelain Enamelware
Primary Hardware
Radios
Recovery of Zinc
Rice Paddy Cultivators
Shallow Well Hand Pumps
Small Steel Melting Plant
Small Steel Rolling Mill
Split Gib-Head Keys and Solid Taper Pins
Stainless Steel Utensils
Storage Bins
Surgical Instruments
Tungsten Carbides
Wire Products

MISCELLANEOUS

Adhesive Tape
Automobile Batteries
Block Ice Making
Dry Cleaning
Souvenirs and Small Jewelry

RUBBER AND LEATHER

Camelback
Children's Shoes
Men's Dress Shoes
Rubber Cement
Rubber Floor Tiles
Rubber Soling
Rubberized Fabric
Small Leather Tannery
Tire Cord Bonding
V-Belts
Women's Shoes

TEXTILES

Cotton Crochet and Knitting Yarns
Cotton Yarn
Hooked Rugs
Jute Yarn
Nylon Hosiery
Surgical Cotton
Wool Scouring
Woolen Yarn
Worsted Yarns

STONE, CLAY AND GLASS

Asphalt Floor Tiles
Cement
Chalk Whiting

WOOD AND PAPER

Brooms
Boxes and Shooks
Creosoted Wood Products
Flush Doors
Hardwood Parquet Flooring
Lead Pencils
Paper Bags
Plywood
Refrigerated Walk-In Coolers
Sensitized Papers
Wood Wastes