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NUCLEAR DIVISION

POST OFFICE BOX X
OAK RIDGE, TENNESSEE 37830

ORNL-MIT-132

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SUBJECT: Energy Expenditures Associated with the Production and Recycle of Metals

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ABSTRACT

Since the presently used resources of our structural metals are being depleted, the equivalent coal energy requirements associated with the production of Mg, Al, Fe, Cu, and Ti metals for varying grades of ore deposits have been evaluated. Future energy requirements for Mg and Fe production will remain essentially constant at 91,000 kwh/ton and 3600 kwh/ton, respectively. Use of poorer grade bauxite ores will not significantly change the energy requirements for Al (∿55,000 kwh/ton); however, eventual use of clays and anorthosite will increase the consumption of energy by more than 35%. The energy requirements for Cu and Ti are 13,530 and 126,300 kwh/ton, respectively. Since both Cu and Ti have limited resources, energy expenditures will increase considerably as poorer grade ores must be used.

Recycle of Cu and Ti from scrap metal requires 1560 and 39,000 kwh/ton, respectively, which is significantly lower than that required to process the metals from their virgin ores. Sulfuric acid, gold, silver, selenium, and tellurium are the principal by-products from copper ores, while zirconium and pig iron can be recovered from titanium deposits. The energy requirements associated with the recovery of these by-products have also been evaluated.

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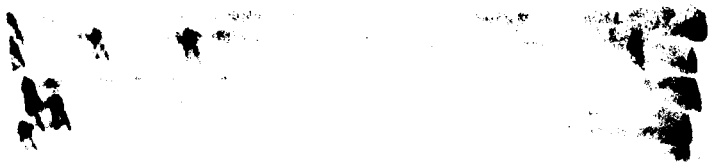

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1. SUMMARY

As part of the NSF Environmental Program, the Materials Resources and Recycle Team is involved in the assessment of materials management. One aspect involves the evaluation of the total energy expenditures in the production and recycle of important structural metals. In this study the energy requirements associated with the production of magnesium, aluminum, iron, copper, and titanium metals from their virgin ores was estimated. Energy requirements for the recovery of by-products and the recycle of copper and titanium were also studied.

Table 1 summarizes the results in terms of equivalent coal energy requirements (kwh/ton of metal) associated with the production and recycle of metals. Energy requirements for Mg production will stay essentially constant in the future (~91,000 kwh/ton) because of its infinite resource in sea water. Use of low grade bauxite ores (~30% Al_2O_3) in the future will not increase energy requirements by more than 16% for Al production (from 51,470 to 59,540 kwh/ton). However, use of poor grade alumina slags and anorthosite will result in 30-40% higher energy expenditures. Although the high grade hematite ores are almost completely exhausted for the production of pig iron, the present use of vast U.S. reserves of magnetic taconites increases the energy requirements only 12% (~3180 to 3560 kwh/ton). If some of the other ores like laterites and specular hematites are employed, energy consumption in their processing can increase to as much as 5200 kwh/ton. For copper production the quality of the mined ore is rapidly falling (from 4% to less than 1%), and use of low grade ores will involve significantly higher mining and milling energies and may increase total energy expenditures by 75% (from 13,530 for a 1.0% Cu ore to 24,760 kwh/ton for a 0.3% Cu ore). Since high grade rutile (TiO_2) ores for titanium production are scarce, use of other minerals containing ilmenite ($FeTiO_3$) will increase energy expenditures by 20%. Ultimate use of the low titanium bearing soils can result in a 72% rise in the energy requirement over that for rutile.

Energy requirements for the recycle of copper and titanium are 1560 and 39,000 kwh/ton, respectively. Potentially, 75% of the copper produced is recyclable, but titanium recycle is minimal since 90% of its usage is dissipative. Valuable by-products from copper production are sulfuric acid, gold, silver, selenium, and tellurium. Zirconium and pig iron are the principal by-products obtainable from titanium processing. The energy requirements for the recovery of these by-products have also been evaluated.

2. INTRODUCTION

One of the major causes of the environmental crisis and the rapid depletion of our raw materials is the mismanagement of physical resources from the viewpoint of total societal benefit (1). At ORNL the Material Resources and Recycle Team of the NSF Environmental Program is involved in the assessment of materials management. One aspect of the program is to

Table 1. Summary of the Energy Requirements for The Production and Recycle of Metals

Metal	Ore or Main Source	Equivalent Coal Energy (kwh/ton metal)
Magnesium	Sea water	90,930
Aluminum	Bauxite (50-30% Al_2O_3)	51,470 - 59,540
	Clays	65,972
	Anorthosite	72,360
Iron	High grade hematite	3,180
	Magnetic taconites	3,560
	Iron laterites	5,180
Copper	1% sulfide ore	13,530
	0.3% sulfide ore	24,760
	98% Cu scrap recycle	590
	Impure Cu scrap recycle	1,560
Titanium	High grade rutile	126,280
	Ilmenite bearing minerals, e.g., sands, rocks, etc.	150,120 to 157,080
	High grade Ti soils	206,750
	Ti scrap recycle	39,000

determine a priority or Materials Criticality Index (MCI), which should provide a measure of the urgency of environmental and conservation incentives for recycling a particular material, developing substitution technology or implementing managerial changes. Included in this index are such elements as: energy expenditures, availability, demand, and environmental damage by recycle.

In the distant future the only major structural metals which will not have an availability problem are magnesium (Mg), iron (Fe), and aluminum (Al). Sea water containing 0.13% Mg is an essentially limitless and homogeneous source of Mg. Al and Fe have several very large ore deposits, though they are limited. As the resources of bauxite (Al) and hematite and magnetite (Fe) are depleted, poorer grade alumina clays and iron ores, taconites and ferruginous laterites, will have to be employed. For both elements, however, the recovery will be influenced adversely by the presence of increasing amounts of silica and other impurities.

As the present resources of most metals are gradually depleted, all other structural metals will become increasingly costly and their usage will be restricted to unsubstitutable or non-dissipative uses. Copper (Cu) and titanium (Ti), a refractory metal, are two typical elements with limited availability. Copper is chiefly found in low grade porphyry ores (0.3 to 1.2%); and presently in the U.S. about 50% of the total copper used is recycled. Although titanium is the ninth most plentiful element (0.4% abundance in earth's crust), the major ores (rutile TiO_2 and ilmenite $TiFeO_3$) are not unlimited. Alternate sources are not satisfactory for two reasons: (1) they are too dilute and (2) they contain several other metallic elements which are difficult to separate. Since 90% of the Ti is consumed as pigments, economic recycle is unfeasible.

The objectives of this study were to evaluate the energy requirements for:

1) Production of magnesium, aluminum, iron, copper, and titanium metals from their virgin ores.

2) Recovery of co-products and by-products in the processing of copper and titanium metals.

3) Recovery of copper and titanium from scrap metal.

3. APPROACH

For each of the five metals (Mg, Al, Fe, Cu, Ti) the analysis was divided into the following categories:

1. A critical evaluation of the important ores, their availability, and potential reserves.

2. A study of the mining, beneficiation, and chemical processing of the ores to yield the final product metal.

3. Calculation of the energy requirements for the individual steps in the production of the metal from their virgin ores.

The energy expenditure (additional) in the recovery of by-products in the production of copper and titanium was calculated. Recycle of the titanium and copper from various forms of scrap metal was studied and the energy requirements estimated.

Three forms of energies were calculated:

1. The Gibbs free energy change, ΔF°, for the overall process was calculated assuming a standard state for all reactants and products as 25°C, 1 atm pressure, and their respective states of aggregation (solid, liquid, or gas). The Gibbs excess free energy of mixing of the ore was assumed to be zero in the calculation of free energies of the products and reactants. ΔF° was calculated since it is a direct measure of the minimum theoretical work or energy needed to convert one mole of the reactants to products.

2. The total energy requirements were defined as the direct summation of all the different energies required in the production or recycle of the metal irrespective of the form, electrical, coal, gas, steam, or of the temperature of operation. This was expressed as kwh per ton of refined metal.

3. The equivalent coal energy was calculated to facilitate a direct comparison of the energies involved in the various processes. In the calculation of this equivalent coal energy the following assumptions were made. Since the overall efficiency of the most modern power stations is 40%, a factor of 2.5 was used to convert electrical to equivalent coal energy (3). An equivalent coal energy of 1.25 kwh was assumed equal to 1.0 kwh of steam since steam generators are generally 80% efficient (2). The energy efficiencies of all other fossil fuels (gas and oil) have been considered to be nearly equivalent; i.e., one kwh of gas or oil = one kwh of coal energy. If a raw material was utilized in the process, an equivalent coal energy associated with the production of that material from natural resources was included; e.g., since lime is used as a flotation agent in copper beneficiation, the energy to produce lime from limestone was added. No transportation energy expenditure for either raw materials or refined metal was included, and processing plants were assumed to be ideally located.

To aid in comparison the cost of the total energy consumed has also been calculated. In making these estimates, the utility prices shown in Table 2 were assumed; they were typical 1971 rates employed by most large industries (3). However, it should be noted that these prices can vary by as much as 50% depending on the geographical location of the consumer.

Table 2. Cost of Utilities Used in the Calculation of Energy Costs

Price ($/kwh)	Source or Type of Energy
0.005	electricity
0.001	coal
0.0015	steam
0.00083	gas

4. MAGNESIUM (Mg)

Magnesium constitutes 2.5% of the earth's crust making it the sixth most abundant chemical element; it is the third most abundant structural metal being exceeded only by aluminum and iron. Magnesium, a silvery white metal with a density two-thirds that of aluminum, has become well known as the world's lightest structural metal. Use for magnesium and magnesium alloys can be divided into two types, structural and non-structural. In the first category the main uses are in the manufacture of aircraft engines and structures, guided missiles, materials-handling equipment, and textile and printing machines. Non-structural uses of magnesium include its application as a consumable anode in cathodic protection of steel and an alloying element in aluminum, zinc, and certain other non-ferrous alloys. Magnesium is also used as an oxygen scavenger in the manufacture of nickel and copper alloys. The total consumption of magnesium in the United States is expected to increase 7 to 8% per year and reach 85,000 tons in 1971 and 170,000 tons in 1980 (M-9).

4.1 Magnesium Ores and Resources

Magnesium is produced from three raw material sources: (1) sea water, (2) mineral deposits such as dolomite ($MgCO_3$, $CaCO_3$), magnesite ($MgCO_3$), and brucite [$Mg(OH)_2$], and (3) lake and well brines and evaporite deposits. Sea water which contains about 0.13% magnesium is an essentially limitless source of magnesium. For example it has been calculated that if magnesium were extracted from sea water at the rate of 100 million tons/year for a million years, the magnesium content of sea water would drop to only 0.12%. Dolomite, magnesite, and brucite contain 22, 47.6, and 69% magnesia, respectively. Large dolomite deposits are widely distributed throughout the world, while magnesite and brucite are less abundant, U.S. reserves total around 70 million tons. The recovery of magnesium from evaporites or natural brines of concentration greater than sea water has been of little industrial significance for economic and technological reasons (M-3).

The present U.S. capacity is preponderantly (>80%) based on the extraction of Mg from sea water by the Dow electrolytic process. With the advent of cheap nuclear power and the essentially infinite resources of magnesium in sea water, the electrolytic process will remain the primary route to Mg metal production. Consequently only the energy requirements for the sea water process have been evaluated in this study.

4.2 Dow Sea Water Process

Figure 1 is a schematic flowsheet of the various steps involved in Mg production. Sea water is filtered and mixed with a slurry of calcium hydroxide obtained either from the calcination of oyster shells (rich source of $CaCO_3$) or limestone. If limestone is used, a grinding step is necessary prior to calcination. The magnesium in solution is precipitated as magnesium hydroxide in large thickener or settling tanks. After the $Mg(OH)_2$ slurry ($\sim$17 wt%) is concentrated by filtration, the filter cake is neutralized with hydrochloric acid to form a 14% solution of magnesium chloride. The solution is then evaporated in direct fired evaporators and dryers to form wet $MgCl_2$ granules ($\sim$74 wt %) which are charged to the electrolysis cells.

The $MgCl_2$ is decomposed to Mg metal at the cathode and chlorine gas at the anode of electrolysis cells operating at 6 v and 30,000+ amp. Artificial graphite electrodes are suspended in the fused bath of $MgCl_2$ (1500°F) and serve as anodes. Current efficiencies range from 75-85%, while typical voltage efficiencies are 35-50% depending on cell construction. The chlorine is sent to a hydrochloric acid plant and recycled to the neutralization step (M-10).

4.3 Process Energy Requirements

The energy requirements of the process can be divided into four categories:

1. Sea water pretreatment

   a) Pumping sea water to the processing plant.

   b) Calcination of oyster shells or limestone. If limestone is used, the energy for grinding must be included.

   c) Precipitation and filtration of $Mg(OH)_2$.

2. Evaporation of Water from $MgCl_2$ Solution

   Approximately 5.3 lb of water have to be evaporated per lb of $MgCl_2$ in direct fired evaporators and tray dryers (natural gas).

3. Electrolysis of $MgCl_2$

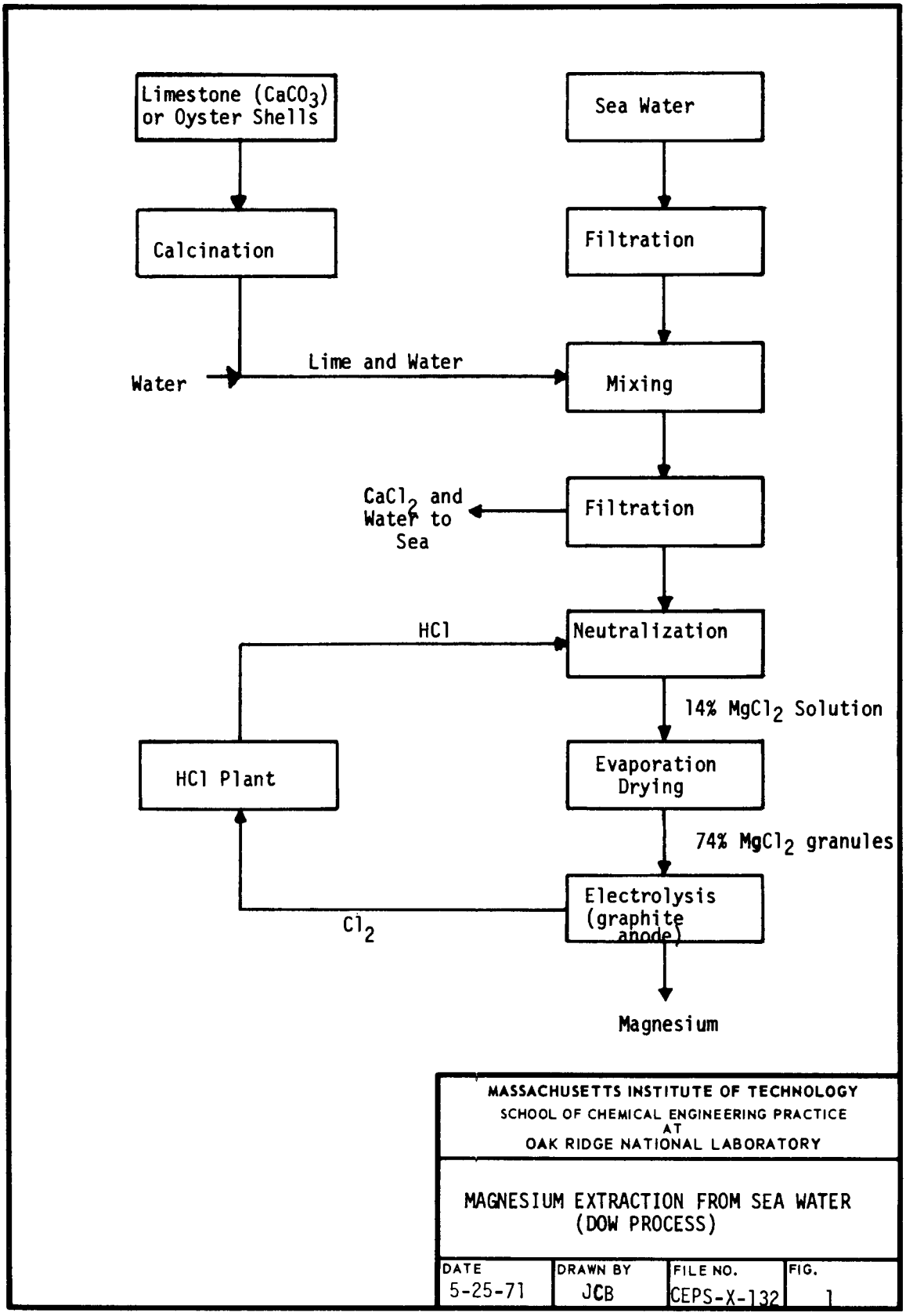
Limestone ($CaCO_3$) or Oyster Shells
Sea Water
Calcination
Filtration
Water
Lime and Water
Mixing
$CaCl_2$ and Water to Sea
Filtration
HCl
Neutralization
14% $MgCl_2$ Solution
HCl Plant
Evaporation Drying
74% $MgCl_2$ granules
Electrolysis (graphite anode)
Cl_2
Magnesium
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY
MAGNESIUM EXTRACTION FROM SEA WATER
(DOW PROCESS)
DATE 5-25-71
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FIG. 1

a) With the present improved cell design, 7 kwh of electricity per lb of Mg metal is a typical operating energy requirement for electrolysis (M-2).

b) The energy for replacing the consumable graphite anode was calculated based on a consumption of 0.1 lb/lb of Mg produced. (M-1)

4. Hydrochloric acid recovery

Currently the hydrochloric acid is being recovered by combustion of chlorine in methane or hydrogen gas. In evaluating the total energy requirements, methane rather than H_2 was used.

$$2Cl_2 + CH_4 + O_2 \longrightarrow 4HCl + CO_2$$

Alternatively the HCl could be produced by the catalytic reaction:

$$Cl_2 + H_2O \xrightarrow{cat} 2HCl + H_2O$$

This route to HCl has not been demonstrated on a large scale; however if technically feasible it would reduce the energy requirements for HCl recycle.

Table 3 gives a summary of the energy requirements for each of the above steps. It is based on the production of one ton of Mg metal. The Gibbs free energy change for the overall process has also been calculated as a measure of the theoretically minimum energy expenditure for producing the metal. The energy requirements for both the limestone and oyster shell processes have been included. Equivalent coal energy assuming coal as the unique energy source has been computed for comparison. The last column in the table indicates the power cost for the process (see costs in Sect. 3). All detailed calculations for the several steps in the process are explained in Appendix 12.1.

5. ALUMINUM (Al)

Aluminum is used in a variety of products because of its low density, high strength-to-weight ratio, resistance to corrosion, high electrical and thermal conductivity, low neutron absorption cross section, non-magnetic and non-sparking properties. Total annual aluminum consumption in the United States in 1963 was around 2.5 million tons and by 1980 it is estimated to be 9.0 million tons (A-8).

Aluminum is the most abundant metal in the earth's crust (7%), and alumina (Al_2O_3) is the principal raw material used for aluminum production. All igneous rock contains silicates of aluminum, and upon weathering or erosion the aluminum usually remains insoluble in the form of an impure aluminum silicate, a clay. However, only bauxite rock qualifies as a

Table 3. Energy Requirements for the Production of Magnesium from Sea Water

(Basis: 1 ton of Magnesium)

Gibbs Free Energy Change, ΔF° = 1233 kwh, Sales Price = $720

	Energy for the Process Using Oyster Shells (kwh)	Energy for the Process Using Limestone (kwh)	Equivalent Coal Energy Using Oyster Shells (kwh)	Power Cost for the Process Using Oyster Shells ($)
1. Sea Water Pretreatment				
a) Pumping	404(E)	404(E)	1,010	5.05
b) Limestone Treatment		126(E)		
Limestone or Oyster Shell Calcination	3,998	3,998	3,998	3.32
c) Mixing, Flocculation, Sedimentation	17(E)	17(E)	42	0.08
2. Evaporation	45,000	45,000	45,000	37.35
3. Electrolysis	14,000(E)	14,000(E)	35,000	70
Electrode Consumption	600(E) + 100	600(E) + 100	1,600	3.10
4. HCl Recovery	4,284	4,284	4,284	3.56
Total	68,403	68,529	90,934	122.46

(E) = electrical energy

commercial source of alumina under the present economic conditions. Although world deposits of bauxite are estimated at 5760 million tons, domestic reserves are only about 50 million tons, but the potential domestic resource in low-grade non-bauxite alumina deposits is practically limitless (A-8). Since poorer grade ores will have to be employed in the near future, the energy requirements have been evaluated for Al production based on three starting materials: bauxite, clay, and anorthosite (a feldspar ore, see Sect. 5.3).

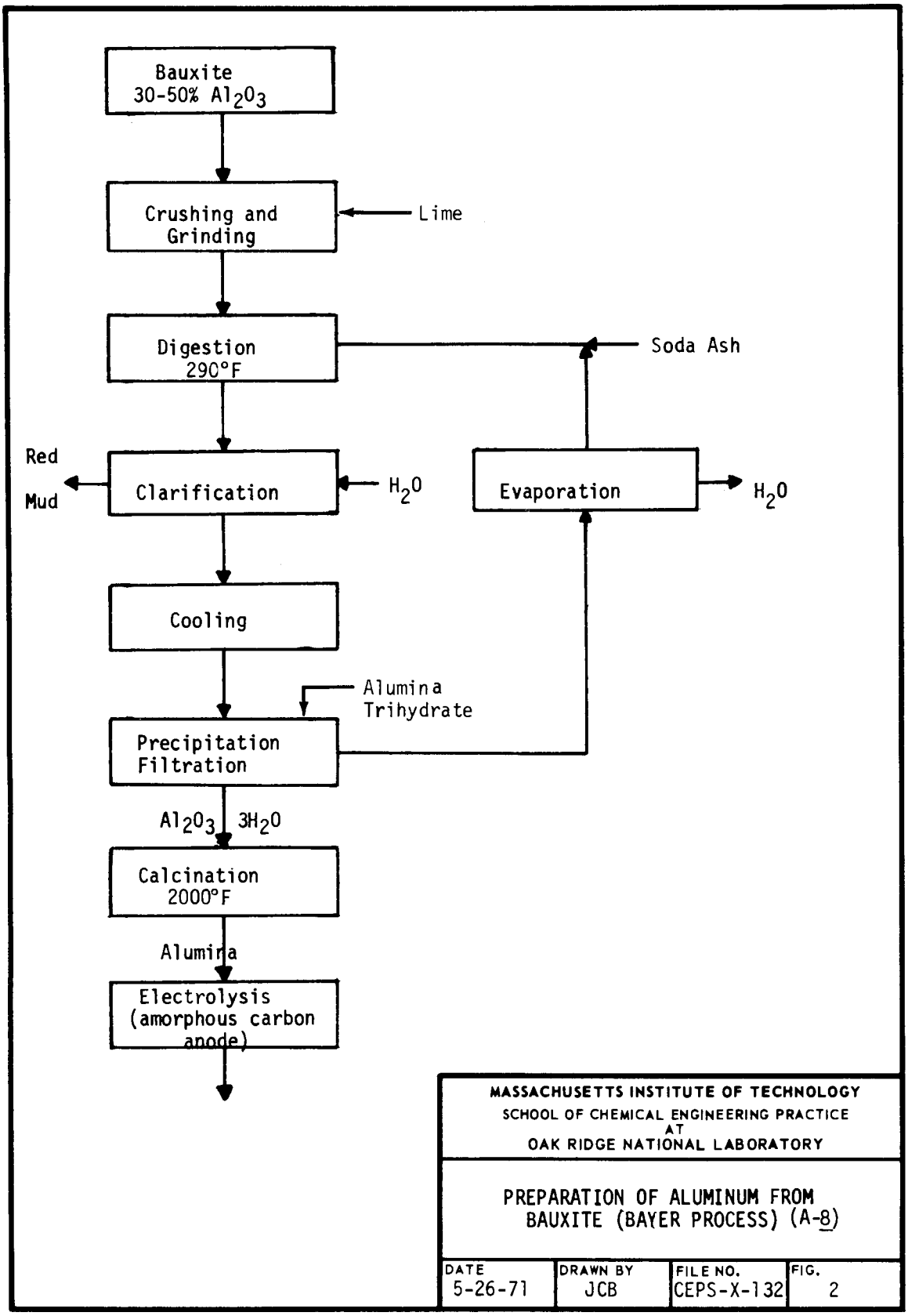
5.1 Aluminum Production from Bauxite Rock

Most of the alumina in bauxite is combined with either three molecules of water per molecule of alumina, $Al_2O_3 \cdot 3H_2O$ or one molecule, $Al_2O_3 \cdot H_2O$. Bauxite can contain 30 to 60% alumina, 1 to 15% silica, and 1 to 30% iron oxide. In this study two typical ores containing 3% silica and 30% and 50% Al_2O_3 have been considered.

Figure 2 is a schematic flowsheet for aluminum production from bauxite by the traditional Bayer process. The process can be divided into three steps: extraction and purification of the hydrated aluminum, calcination (dehydration), and electrolysis of alumina in molten cryolite (sodium alumino fluoride).

Open pit mining accounts for most of the bauxite refined in the United States. The ore is initially crushed to about 2 in. in size. If the bauxite has a silica content greater than 8% but preferably less than 10%, it is generally first beneficiated by washing and jigging before digestion. The alumina is extracted from the bauxite by digestion at elevated temperature (300-400°F) and pressure with a strong caustic soda solution resulting in a sodium aluminate solution and a residue termed "red mud." The red mud consists of silica, iron oxide, titanium oxide, and insoluble aluminum silicate. The pregnant alumina liquor is cooled and seeded with crystals of alumina trihydrate. About half the alumina precipitates over a 36 to 100 hr period as alumina trihydrate. The precipitate is then filtered and washed, while the filtrate consisting of a weak solution of sodium aluminate and caustic soda is recycled after the excess water is evaporated (A-8).

The crystalline alumina trihydrate is calcined in a rotary kiln at 2000°F to remove the water, resulting in pure crystalline alumina. The alumina is then electrolyzed in a molten cryolite bath at a temperature of 1760-1800°F. The reduction cell is made of a carbon-lined box containing a pad of molten cryolite in which the alumina is dissolved. The anode is either a single large block or several small blocks of carbon. The alumina is reduced to aluminum at the cathode, and carbon is oxidized to carbon dioxide at the anode. Current efficiencies range from 85-90% due to material losses of the metal and re-oxidation of Al by the CO_2. Industrial cells have low voltage efficiencies around 40% due to electrode resistance, polarization, and radiation heat losses. As a result the overall power efficiency is approximately 35%, and 7 kwh/lb of Al are needed for a well designed cell (A-8).


Bauxite
30-50% Al_2O_3
Crushing and Grinding
Lime
Digestion
290°F
Soda Ash
Red Mud
Clarification
H_2O
Evaporation
H_2O
Cooling
Alumina Trihydrate
Precipitation Filtration
Al_2O_3 $3H_2O$
Calcination
2000°F
Alumina
Electrolysis
(amorphous carbon anode)
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY
PREPARATION OF ALUMINUM FROM BAUXITE (BAYER PROCESS) (A-8)
DATE 5-26-71
DRAWN BY JCB
FILE NO. CEPS-X-132
FIG. 2

The bauxite containing more than 10% silica must be pretreated by calcination with soda and limestone yielding an insoluble calcium silicate ($CaSiO_2$) which is filtered with the red mud. The remaining process is identical to that described above for the low silica bauxite.

The energy needs for the Bayer Process can conveniently be divided into five categories:

1. Bauxite pretreatment (mining, crushing, grinding, and washing).

2. Digestion of the bauxite and evaporation of excess water. Makeup caustic (lime and soda ash) is specified by silica content (1.2 tons soda/ton of silica).

3. Pumping, clarification, and filtration of the pregnant solution prior to calcination.

4. Calcination of the $Al_2O_3 \cdot 3H_2O$ in a rotary kiln using natural gas as the heat source.

5. Alumina electrolysis and replacement of consumable carbon anodes.

The individual energy breakdown for each of these steps is summarized in Table 4 with detailed calculations in Appendix 12.2. The minimum theoretical work of separation as given by the Gibbs free energy change is 5800 kwh/ton Al. To illustrate the energy requirements of lower grade ores, energies for both a 30% Al_2O_3 and a 50% Al_2O_3 bauxite have been calculated. Equivalent coal energies for the two ores along with an energy cost for the 50% Al_2O_3 are indicated.

The electrolysis of alumina is clearly the single most energy intensive part of the whole process ($\sim$17,500 kwh/ton). Steam requirements for the evaporation and digestion also significantly effect the total energy ($\sim$36%). Steam requirements increase appreciably with poorer grade bauxite; however, this increase is far greater than that due to the mining and beneficiation of the poorer ore. The total energy per ton of Al produced for the 30% Al_2O_3 bauxite is 21% higher than that for the 50% alumina rock. On an equivalent coal basis though, the difference is smaller ($\sim$16%).

5.2 Production of Aluminum Metal from Clay

The expanding aluminum production in the U.S. and the limited resources of domestic bauxite have stimulated an interest in the practicability of methods for the recovery of metallurgical-grade alumina from poorer grade sources such as clay. Clay is a semi-infinite resource for alumina. A typical clay used in this study contains 30% alumina, 3% iron oxide, 50% silica, 15% of material which is lost on ignition (combined with water).

Figure 3 is a schematic flowsheet of the several operations involved in the recovery of Al_2O_3 from clay using the nitric acid process. This

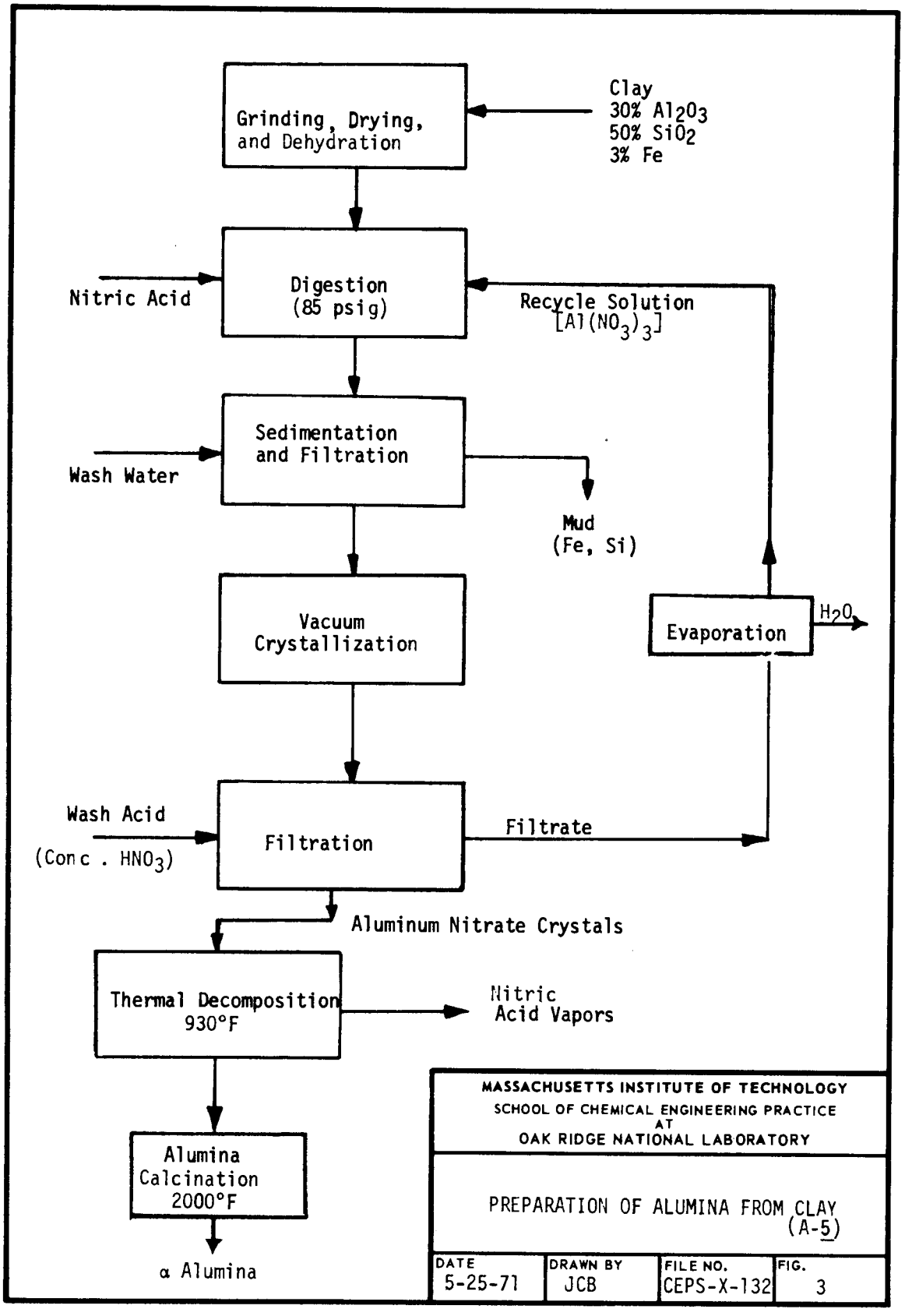
Table 4. Energy Requirements for the Production of Aluminum from Bauxite by the Bayer Process

(Basis: 1 ton of Aluminum)

Gibbs Free Energy, ΔF° = 4400 kwh, Sale price = $550

Steps	Energy Requirements for a 30% Al_2O_3 Bauxite (kwh)	Energy Requirements for a 50% Al_2O_3 Bauxite (kwh)	Equivalent Coal Energy (kwh) 30% Bauxite	Equivalent Coal Energy (kwh) 50% Bauxite	Power Cost for 50% Al_2O_3 Bauxite ($)
1. Bauxite Mining, Crushing, Grinding, and Washing	1,300(E)	500(E)	3,250	1,250	2.5
2. Steam for Evaporation and Digestion	12,306	7,384	15,383	9,230	11.08
3. Pumping, Clarification, and Filtration	83(E)	50(E)	125	208	0.25
4. Calcination of $Al_2O_3 \cdot 3H_2O$	2,281	2,281	2,281	2,281	1.89
5. Electrolysis	14,000(E)	14,000(E)	35,000	35,000	70.0
Anode Replacement (0.5 ton Amorphous Carbon)	3,500	3,500	3,500	3,500	3.5
Total	33,470	27,715	59,539	51,469	$ 89.22

(E) = electrical energy


Grinding, Drying, and Dehydration
Clay
30% Al_2O_3
50% SiO_2
3% Fe
Digestion (85 psig)
Nitric Acid
Recycle Solution $[Al(NO_3)_3]$
Sedimentation and Filtration
Wash Water
Mud (Fe, Si)
Vacuum Crystallization
Evaporation
H_2O
Wash Acid
(Conc . HNO_3)
Filtration
Filtrate
Aluminum Nitrate Crystals
Thermal Decomposition 930°F
Nitric Acid Vapors
Alumina Calcination 2000°F
α Alumina
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY
PREPARATION OF ALUMINA FROM CLAY (A-5)
DATE 5-25-71
DRAWN BY JCB
FILE NO. CEPS-X-132
FIG. 3

process is based on the low solubility of iron in basic aluminum nitrate solutions. Clay, after crushing, grinding, and dehydration, is digested with slightly less than the stoichiometric HNO_3 required to form normal aluminum nitrate. Under these conditions a basic $Al(NO_3)_3$ solution is formed in which iron is insoluble. After filtration the solution is concentrated to crystallize aluminum nitrate monohydrate, leaving a basic $Al(NO_3)_3$ mother liquor which is recycled to the digestion step. These crystals are then washed with concentrated nitric acid and thermally decomposed in the presence of steam to alumina and nitrogen oxides. The alumina is finally calcined at 2000°F to convert it to the alpha form which is then sent for electrolysis as in the Bayer Process

Since no industrial production of aluminum from clay has been achieved, the estimates of the energy requirements shown in Table 5 are based on a preliminary report issued by the Bureau of Mines (A-5). (See Appendix 12.2.3 for details.)

Table 5. Energy Requirement in Al Production from Clay

Basis: 1 ton Aluminum

Steps	Energy Requirement (kwh)	Equivalent Coal Energy (kwh)	Power Cost ($)
Alumina Preparation			
Electricity	204(E)	510	1.02
Steam	9,947	12,434	14.92
Gas	14,228	14,228	11.81
Nitric Acid (0.14 ton)	300	300	0.26
Electrolysis of Alumina			
Electrolysis	14,000(E)	35,000	70
Anode Replacement	3,500	3,500	3.50
Total	42,179	65,972	$101.51

(E) = electrical energy

A comparison of Tables 4 and 5 indicates that when the clays are used, the energy requirements for the alumina beneficiation are considerably higher. A 50% bauxite requires 51,470 kwh/ton of equivalent coal energy compared to 65,972 kwh/ton for clay.

5.3 Production of Aluminum from Anorthosite

The Bureau of Mines also investigated use of other domestic low grade aluminum resources including anorthosite, a feldspar ore $(CaO \cdot Al_2O_3 \cdot 2SiO_2)_x$ $(Na_2O \cdot Al_2O_3 \cdot 6SiO_2)_y$. In this process alumina is extracted by sintering (calcination) of anorthosite with soda ash and limestone. The calcination products are then leached with a dilute sodium carbonate solution to extract the alumina. After the pregnant solution is treated with lime to precipitate any dissolved silica, the solution is carbonated to precipitate alumina trihydrate which is calcined at 2000°F into alumina. The alumina is then electrolyzed according to the conditions of the Bayer process.

The energy requirements estimated by the Bureau of Mines are summarized in Table 6 (a theoretical evaluation). The energy requirements on an equivalent coal basis are approximately 5800 kwh/ton greater than for clay and about 21,000 kwh/ton greater than for a rich bauxite (50% Al_2O_3).

Table 6. Energy Requirements for Aluminum Production by the Anorthosite Process

Basis: 1 ton Aluminum

Steps	Energy Requirements (kwh)	Equivalent Coal Energy (kwh)	Power Cost ($)
Preparation of Alumina			
Electrical Power	1,540(E)	3,840	7.7
Steam	7,825	12,281	14.74
Gas	15,300	15,300	12.69
Soda Ash (0.17 ton)	697	697	.70
Limestone (grinding) (17.6 ton)	695(E)	1,738	3.48
Electrolysis	14,000(E)	35,000	70.00
Anode Consumption	3,500	3,500	3.50
Total	43,557	72,356	$ 112.81

(E) = electrical energy

In summary, the energy requirements for aluminum production will increase in the future as bauxite reserves are depleted and clays and anorthosites are utilized. Energy requirements for clays and anorthosites will be 29 and 40% higher than for the present bauxite ores. However, if a poorer grade bauxite ore (up to 30% alumina and silica < 15%) is readily available, the increase in energy will be less than 16%.

6. IRON (Fe)

Iron (Fe) is the second most abundant structural material in the earth's crust and the fourth most common element (3.5% abundance). The greatest use is for structural steels, and cast iron and wrought iron products. Magnets, dyes, and abrasives are among the other uses of iron. Production of pig iron in the United States has been increasing at the rate of 1.6% annually, and is expected to reach 93 million tons by 1980 (I-10). Total world resources of iron ores containing 40-50% Fe have been estimated at 5.5×10^{11} tons. Although iron is very abundant, the supply of high grade ores requiring no beneficiation except coarse crushing (hematite averaging 58-60% Fe) is now very limited. In the last several years the iron industry has been developing technology to use poorer ores such as magnetic taconites (32-40%) and laterites (~45-47% Fe). However, use of these alternative resources may increase the energy requirements and economics of iron production.

6.1 Production of Iron from Virgin Ores

Iron is extracted from the ore by pyrometallurgical processes. At temperatures of 1290-2015°C iron oxides such as hematite (Fe_2O_3) and magnetite (Fe_3O_4), the principal iron-bearing minerals, are readily reduced to metallic iron. The reduction is carried out in a blast (93%), open hearth (6%), or electric smelting furnace (I-10). Carbon (coke) is not only the reducing agent but also the primary heat source (65%) for the blast furnace. Limestone or lime is generally added to flux the numerous impurities into a free flowing slag which can be easily tapped. The blast furnace produces pig iron containing about 3-4% carbon and manganese, silicon, sulfur, and phosphorous totaling 1.65%. This pig iron is rather brittle and has poor strength and ductility; therefore, most of it is converted to steel, the principal end product.

6.2 Virgin Ores of Iron and Their Beneficiation

The most important minerals of iron are hematite (Fe_2O_3), magnetite (Fe_3O_4) and limonite ($Fe_2O_3 \cdot H_2O$) (I-5). Hematite and limonite, a hydrated form of hematite, are non-magnetic. These minerals and the ores which contain them vary vastly in both physical and chemical properties so that a common beneficiation process is rarely possible. The important iron ores

are high grade hematite ores, magnetic taconites, non-magnetic taconites, specular hematites, and iron laterites (I-5).

Most open-pit mines have similar mining procedures. Ammonium nitrate and fuel oil slurries are employed in blasting the deposits (I-7). Ore chunks are then transported to a beneficiation plant to upgrade the crude ore to 60-65% iron and approximately 8% SiO_2. The beneficiated ore is then finely ground and pelletized (1 to 2 in.) before charging to the blast smelting furnaces (I-10). A brief description of the important ores and their beneficiation is presented below:

1. High Grade Hematite Ores (58-59% Fe). These ores are rich in Fe_2O_3 and require little or no beneficiation before smelting (I-5). Hematite reserves have been nearly exhausted; therefore lower grade magnetic taconites have been increasingly used since 1960.

2. Magnetic Taconites. At the present time magnetic taconites are the primary ores (~80%) of the iron and steel industry. Reserves of taconites are enormous; the Lake Superior district has approximately 1×10^{11} tons of ore (I-10) averaging 22-35% Fe. The silica content is high, 40-50% SiO_2. All magnetic taconites have a fine-grained, dense, hard structure.

Figure 4 is a flowsheet of a typical beneficiation plant for magnetic taconites. The crude, hard taconite is ground to -325 mesh in a series of crushers, each followed by a magnetic separation. The magnetite from the ore is thus readily separated. The concentrate is then pelletized at 2000°F in a furnace using propane as the fuel. A 95% recovery of the magnetite is obtained and 3.2 tonsof crude ore generate a ton of pellets assaying 63% Fe and less than 8% SiO_2 (I-7).

3. Non-Magnetic Taconites. These non-magnetic ores contain hematite and limonite averaging 28-40% Fe (I-5). Beneficiation can be obtained in dry, high intensity separators (~20,000 gauss field strength) which permit separation of hematite from materials of lower magnetic susceptibility. A simplified flowsheet for the beneficiation is shown in Fig. 11 in Appendix 12.3.3.

4. Specular Hematites. Specular hematites are composed of steel gray crystalline hematite in a matrix of granular quartz, averaging 40-50% iron and about 50% SiO_2. The ore is crushed to a -48 mesh size and charged to a flotation separator which uses 1.0 to 1.8 ton of fatty acid per ton of ore. The clarified concentrate is dried at 220°F and pelletized at 2000°F (I-1). A schematic flowsheet for the process is given in Fig. 12 in Appendix 12.3.3.

5. Iron Laterites. Laterites are hydrated iron oxides containing 40% or more iron (I-4), and they constitute approximately 20% of the total iron ore reserves of the world. The importance of laterites will increase considerably because they contain other valuable elements (I-4) such as nickel (0.8-1%), chromium (1%), and alumina (2-7%) which can be recovered in the iron beneficiation.

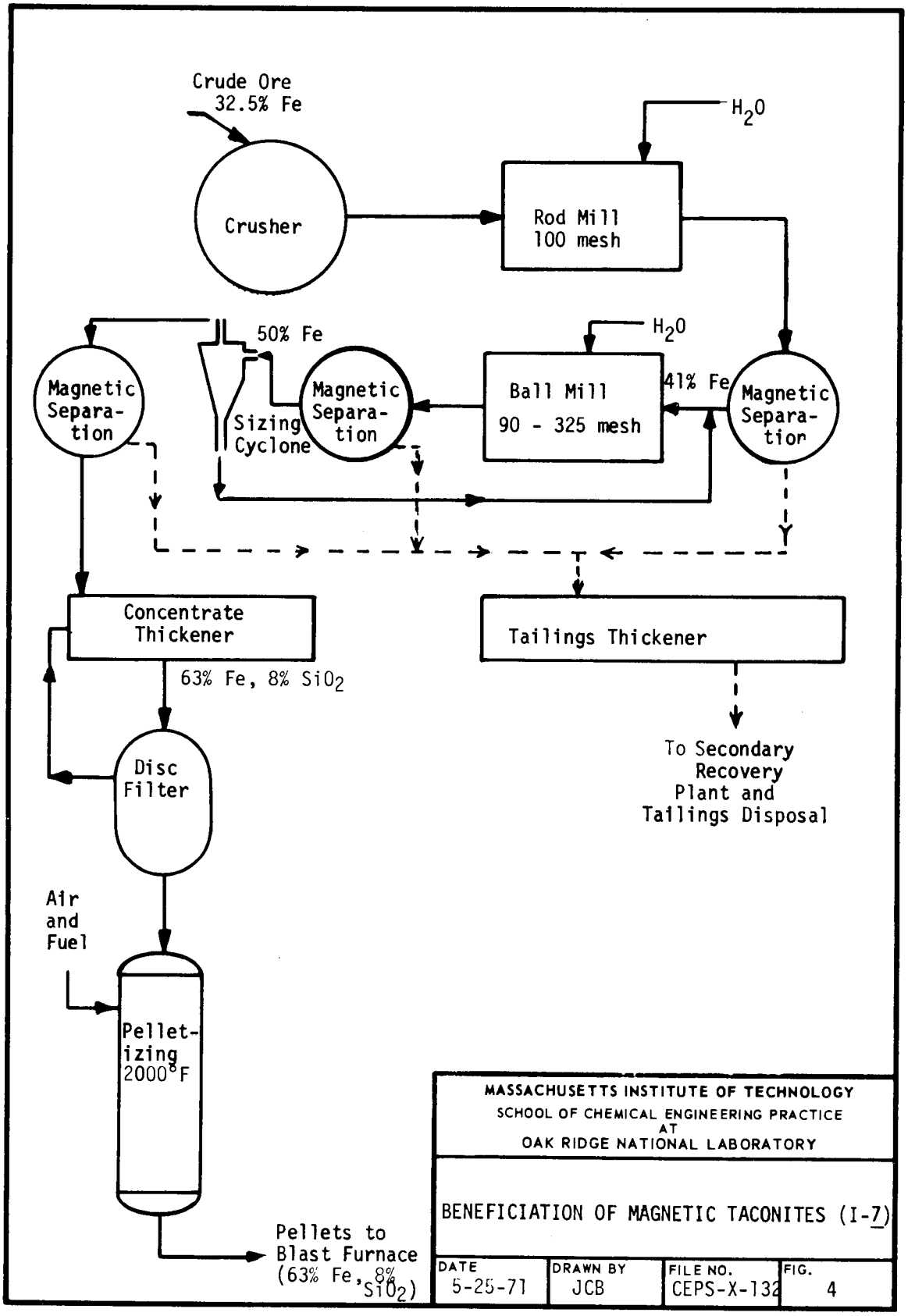

Crude Ore
32.5% Fe
Crusher
H_2O
Rod Mill
100 mesh
H_2O
50% Fe
Magnetic Separation
Sizing Cyclone
Magnetic Separation
Ball Mill
90 - 325 mesh
41% Fe
Magnetic Separation
Concentrate Thickener
63% Fe, 8% SiO_2
Tailings Thickener
To Secondary Recovery Plant and Tailings Disposal
Disc Filter
Air and Fuel
Pelletizing 2000°F
Pellets to Blast Furnace (63% Fe, 8% SiO_2)
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY
BENEFICIATION OF MAGNETIC TACONITES (I-7)
DATE 5-25-71
DRAWN BY JCB
FILE NO. CEPS-X-132
FIG. 4

Figure 13 in Appendix 12.3.3 gives a flowsheet for upgrading iron laterites. The ore is crushed and ground to a -325 mesh followed by a roasting step to convert the non-magnetic Fe_2O_3 to magnetic Fe_3O_4. The iron fraction is then recovered from the gangue material by a magnetic separation. Since nickel is also magnetic, it will have to be subsequently removed by a high intensity magnetic separator from the iron fraction. The concentrated iron ore is then pelletized at 2000°F.

6.3 Chemical Reduction of Beneficiated Ore

The reduction can be achieved in a blast furnace or an electric smelting furnace:

1. Blast Furnace. The blast furnace is used to produce approximately 93% of the total pig iron. The iron ore pellets, coke, and limestone are charged to the top of the furnace, and a blast of hot air and fuel at 2000°F is blown in at the bottom. Per ton of pig iron produced, 1.52 ton of ore pellets, 0.027 ton scrap iron (optional), 0.6 ton coke, and 0.26 ton limestone are consumed (I-1, 2, 5). The coke supplies the energy for smelting of the iron and provides the carbon monoxide for reducing the ore. The chemistry of the individual reactions is complex; however, the following relations are representative of the overall process:

$$C + \frac{1}{2}O_2 \longrightarrow CO_2, \quad \Delta H° = -8255.08 \text{ kwh/ton C}$$

$$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2, \quad \Delta H° = 624.6 \text{ kwh/ton Fe}$$

$$2Fe_3O_4 + 2CO \longrightarrow 6FeO + 2CO_2, \quad \Delta H° = 34.17 \text{ kwh/ton Fe}$$

$$6FeO + 6CO \longrightarrow 6Fe + 6CO_2, \quad \Delta H° = -57.37 \text{ kwh/ton Fe}$$

Approximately one third of the coke is utilized for chemical reduction. The limestone fluxes with the sulfur and ore gangue in the charge. The slag which is lighter than the molten pig iron is then tapped from the furnace. The finished pig iron typically contains 3-4% C, 0.8% Si, 0.8% manganese, 0.03% sulfur, and 0.016% phosphorous (I-1). Table 17 in Appendix 12.3.1.2 gives typical material and energy consumptions for a blast furnace.

2. Electric Smelting Furnace. Electrical smelting of iron ores is gaining popularity in regions with low cost electric power. The advantages of the process include the use of low grade coke or mixtures of coke and coal as a reducing agent, lower coke consumption, and flexibility in handling large amounts of recycle metal scrap. The major drawbacks are relatively lower production rates (I-1) (93 tons/day compared to 4400 tons/day

in the blast furnace), and higher consumptions of electrical energy per ton of pig iron. The reduction reactions involved in the electric furnace are the same as in the blast furnace. Table 18 in Appendix 12.3.1.2 gives a typical set of operating data for an electrical furnace.

6.4 Energy Requirements

The energy requirements for the production of pig iron from several important virgin ores are shown in Table 7. The detailed calculations involved in each step are listed in Appendix 12.3. The energy requirements for mining and beneficiation (to produce a concentrate of 63% Fe and 8% SiO_2) depend strongly on the type of ore used, whereas the energy for chemical reduction is the same for all ores. High grade hematites consume only 60 kwh/ton Fe compared to 430 kwh/ton Fe for the magnetic taconites, and 2060 kwh/ton Fe for the iron laterites. Currently most of the iron produced is from magnetic taconites; however, future use of low grade ores like laterites would result in a significant increase in the beneficiation energy requirements,primarily the roasting step. The reaction involved in roasting is,

$$3Fe_2O_3 + CO \xrightarrow{1500°F} 2Fe_3O_4 + CO_2$$

which consumes 1180 kwh/ton Fe (I-1, 5).

Pelletization of magnetites (e.g., in taconites) consumes much less energy (~225 kwh/ton) than for hematites because the heat released during the oxidation of Fe_3O_4 to Fe_2O_3 supplies a substantial part of the total energy requirements. The beneficiation energy requirements for non-magnetic taconites and specular hematites are nearly double that for taconites because of the beneficiating step.

The equivalent coal energy consumption for a blast furnace is 3119 kwh/ton compared to 8238 kwh/ton for the electric smelting furnace. The energy consumption figures in Table 7 for the hematite ores and magnetic taconites are based on existing operations in the iron industry. For the other three ores the energy requirements were calculated based on cited literature. Future developments in processing technology may significantly reduce these figures; e.g., prereduction of the pellets prior to charging to the blast furnace has been claimed to reduce energy needs by 800 kwh/ton Fe (I-9).

The total energy requirement for iron production from taconites is 3560 kwh/ton Fe compared to 3180 kwh/ton Fe for the high grade hematite ores, an increase of only 12%. Energy requirements for the non-magnetic taconites and specular hematites are still higher, 4050 kwh/ton Fe, while the laterites consume 5180 kwh/ton Fe of equivalent coal energy. Table 8 gives the cost of energy for iron production from several ores. Energy costs using taconites are not appreciably different from those based on the

Table 7. Energy Requirements for the Production of Pig Iron from Various Virgin Ores

Basis: 1 ton Iron, Gibbs Free Energy Change, ΔF° = -941 kwh

	High Grade Hematites	Magnetic Taconites (32.5% Fe, 43% SiO_2)	Non-Magnetic Taconites (28% Fe, 43% SiO_2)	Specular Hematites (38% Fe, 50% SiO_2)	Iron Laterites (48% Fe, 0.8% Ni
1. Mining and Beneficiation (to 63% Fe)					
Drilling and Blasting	6	6	6	8	8
Stripping	5(E)	5(E)	5(E)	5(E)	3.5(E)
Crushing	8(E)	11(E)	11(E)	9(E)	7(E)
Grinding	-	53(E)	68(E)	20(E)	20(E)
Gravity Concentration (including flotation)	-	-	15(E)	18(E)	-
Drying	-	-	45	60	-
Magnetic Concentration	-	5(E)	-	-	4(E)
High Intensity Electrostatic or Magnetic Separation	-	-	18(E)	-	25(E)
Roasting	-	-	-	-	1180
Pelletizing	-	225	698	698	698
Miscellaneous (tailings disposal, pumping, etc.)	9(E)	9(E)	9(E)	12(E)	9(E)
Total	22(E) + 6	83(E) + 231	126(E) + 703	64(E) + 766	69(E) + 1886
Equivalent Coal Energy	61	439	1018	926	1057
2. Chemical Reduction					
Blast Furnace	3119	3119	3119	3119	3119
Equivalent Coal Energy	3119	3119	3119	3119	3119
Electric Furnace	2200(E) + 2738	2200(E) + 2738	2200(E) + 2738	2200(E) + 2738	2200(E) + 2738
Equivalent Coal Energy	8238	8238	8238	8238	8238
3. Total Energy Requirements					
Via Blast Furnace	22(E) + 3125	83(E) + 3350	126(E) + 3822	64(E) + 3885	69(E) + 5005
Equivalent Coal Energy	3180	3558	4137	4045	5176
Via Electric Furnace	2222(E) + 2744	2283(E) + 2969	2326(E) + 3441	2264(E) + 3504	2269(E) + 4624
Equivalent Coal Energy	8299	8677	9256	9164	10,295

(E) = Electrical Energy

now scarce hematite ores. Since U.S. reserves of taconites are almost limitless ($\sim 10^{11}$ tons), it can be concluded that energy requirements for iron production will remain essentially constant. However, eventual use of the laterites would result in an increase in energy requirements by approximately 45%.

Table 8. Power Costs Associated with the Production of Pig Iron From Virgin Ores (Blast Furnace Process)

Basis: $/ton Fe

	High Grade Hematite Ores	Magnetic Taconites	Non-Magnetic Taconites	Specular Hematites	Iron Laterites
Mining and Beneficiation	0.08	0.61	1.28	0.94	2.22
Blast Furnace	3.12	3.12	3.12	3.12	3.12
Total	$ 3.20	$ 3.73	$ 4.40	$ 4.06	$ 5.34

7. COPPER (Cu)

Copper is one of the most important non-ferrous metals. Its high electrical and thermal conductivities, corrosion resistance, good ductility, and malleability are responsible for its important and diverse use in industry. In addition copper is non-magnetic and is easily finished by plating or lacquering; it can be welded, brazed, and soldered satisfactorily. Approximately half of all copper consumed is for electrical applications. World reserves of the metal have been estimated at 212 million tons. World production has climbed steadily from 3.1 million tons in 1954 to 5.2 million tons in 1963, and is estimated to be 12.0 million tons in 1971 (C-16). U.S. production of copper totaled 2.75 million tons in 1970 (C-4).

Although the world is plentifully endowed with copper, the six principal producing areas constitute 85% of the worlds measured and indicated reserves. Copper comes primarily from porphyry deposits with average grades of 1.1 to 1.3% copper; however, U.S. grades now run around 0.65%. As the demand of copper has increased significantly over the years, considerable research in mining and metallurgical techniques has yielded economic techniques for beneficiating poorer grade ores (as low as 0.3-0.4%). Native copper, once widespread in the United States, is now mined only in Michigan. These resources, however, are very limited ($\sim$67,000 tons) (C-9).

In addition to copper, nickel, zinc, and arsenic, several important by-products like silver, gold, selenium, tellurium, cobalt, and molybdenum are recovered from the copper ore. These metals are generally recovered in the

refining step. Sulfuric acid is often produced from the SO_2 from the smelting step for the copper plants using sulfide rather than the oxide ores (see Fig. 5).

An important part of the U.S. reserve is the ever-increasing reclaimable copper scrap which constitutes approximately one fourth of the total U.S. supply. In 1970 0.535 million tons or approximately 19% of the total copper production was recycled in the U.S. (C-4). Currently 39% of the domestic copper production is used for copper alloys like brass and bronze (C-10) containing 60-99% copper (see Fig. 5).

7.1 Processing of Copper from Sulfide Ores

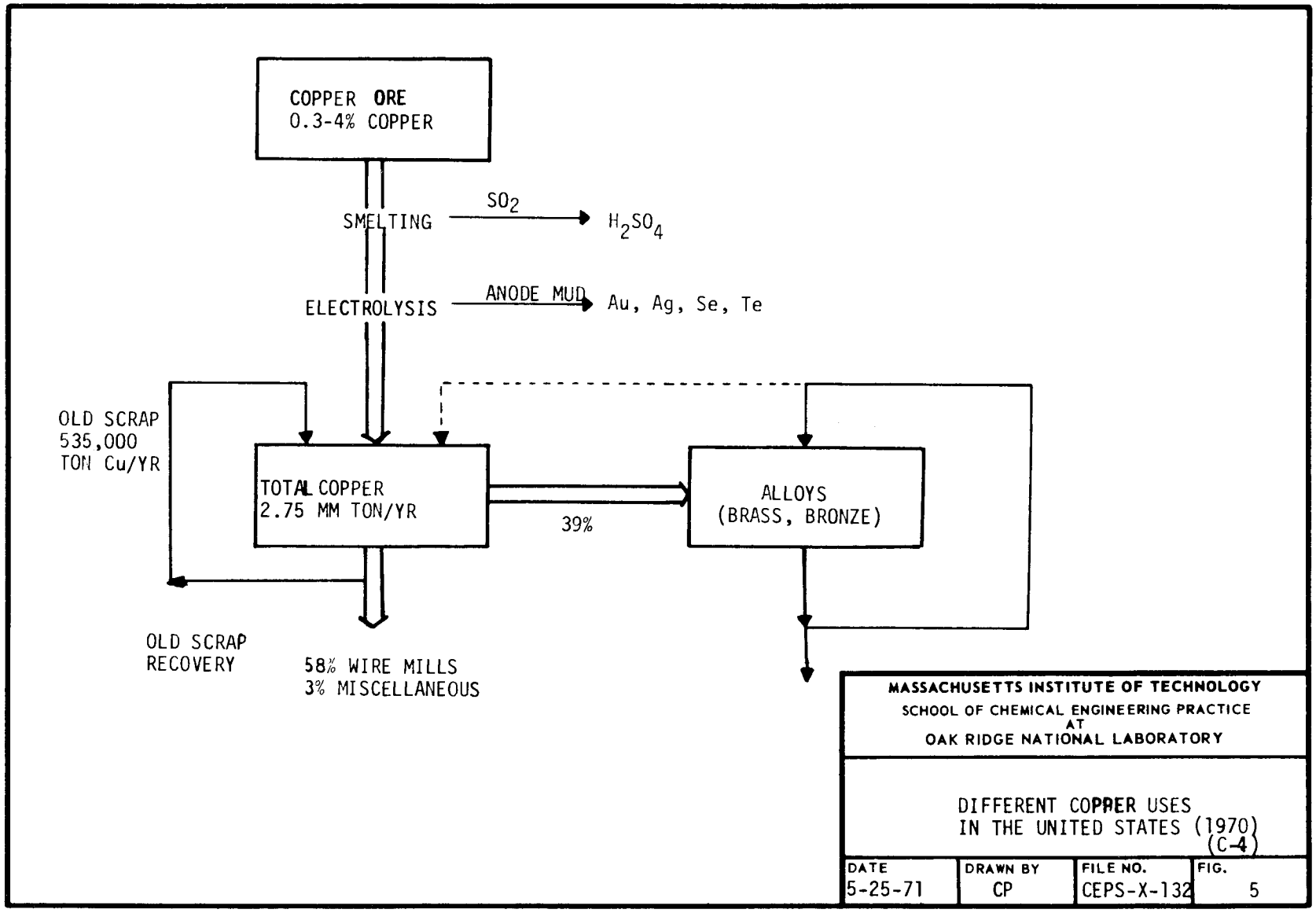
The production of copper can be divided into three convenient steps: (1) mining and milling, (2) smelting, and (3) refining. Although minor variations and improvements will be made in the process, it is expected that the major process steps, as described schematically in Fig. 6, will remain even for poorer grade ores (<0.8%).

1. Mining and Milling. Open pit mining accounted for 74% of the copper and 81% of the ore mined in the United States in 1963 (C-16). After the ore has been drilled and blasted, it is transported to the beneficiation plant where it is crushed to an approximate size of 1 to 2 in. followed by a grinding step.

The method of separating copper minerals from the gangue is determined by the chemical form, size, density, and surface characteristics. The most commonly used practice involves a froth flotation operation. The finely ground ore is agitated in water with air. Surfactants are added to cause the desired minerals to adhere and rise to the surface where they are removed in the froth. Other minerals remain suspended in the bulk fluid. More than 90% of the copper is recovered (C-16), and the concentrate contains 20-30% copper and 15-30% iron.

2. Smelting. In the smelting copper is separated from iron, sulfur, and gangue in two steps: roasting in a reverberatory furnace and converting. In the reverberatory furnace fired with oil, gas, or pulverized coal, the copper and iron in the molten charge react to form copper sulfide and iron oxide. The iron oxide rises to the top of the molten charge with the silica in the ore to form a slag. Any excess iron sulfide remains with the copper sulfide in a molten solution called copper matte. The copper matte containing 30-45% Cu is charged to the converter to form blister copper in two steps: oxidation of the remaining ferrous sulfide and separation as slag, and oxidation of the copper sulfide to blister copper with a purity >99%.

3. Refining. Copper produced by smelting is too impure for most applications and requires further refining. The molten blister copper is transferred to a fuel fired furnace where the copper is further oxidized removing more impurities and cast as anodes. When most of the oxidation is completed, green wood logs are thrust into the molten metal to scavenge


COPPER ORE
0.3-4% COPPER
SMELTING
SO_2
H_2SO_4
ELECTROLYSIS
ANODE MUD
Au, Ag, Se, Te
OLD SCRAP
535,000
TON Cu/YR
TOTAL COPPER
2.75 MM TON/YR
39%
ALLOYS
(BRASS, BRONZE)
OLD SCRAP
RECOVERY
58% WIRE MILLS
3% MISCELLANEOUS
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY
DIFFERENT COPPER USES
IN THE UNITED STATES (1970)
(C-4)
DATE
5-25-71
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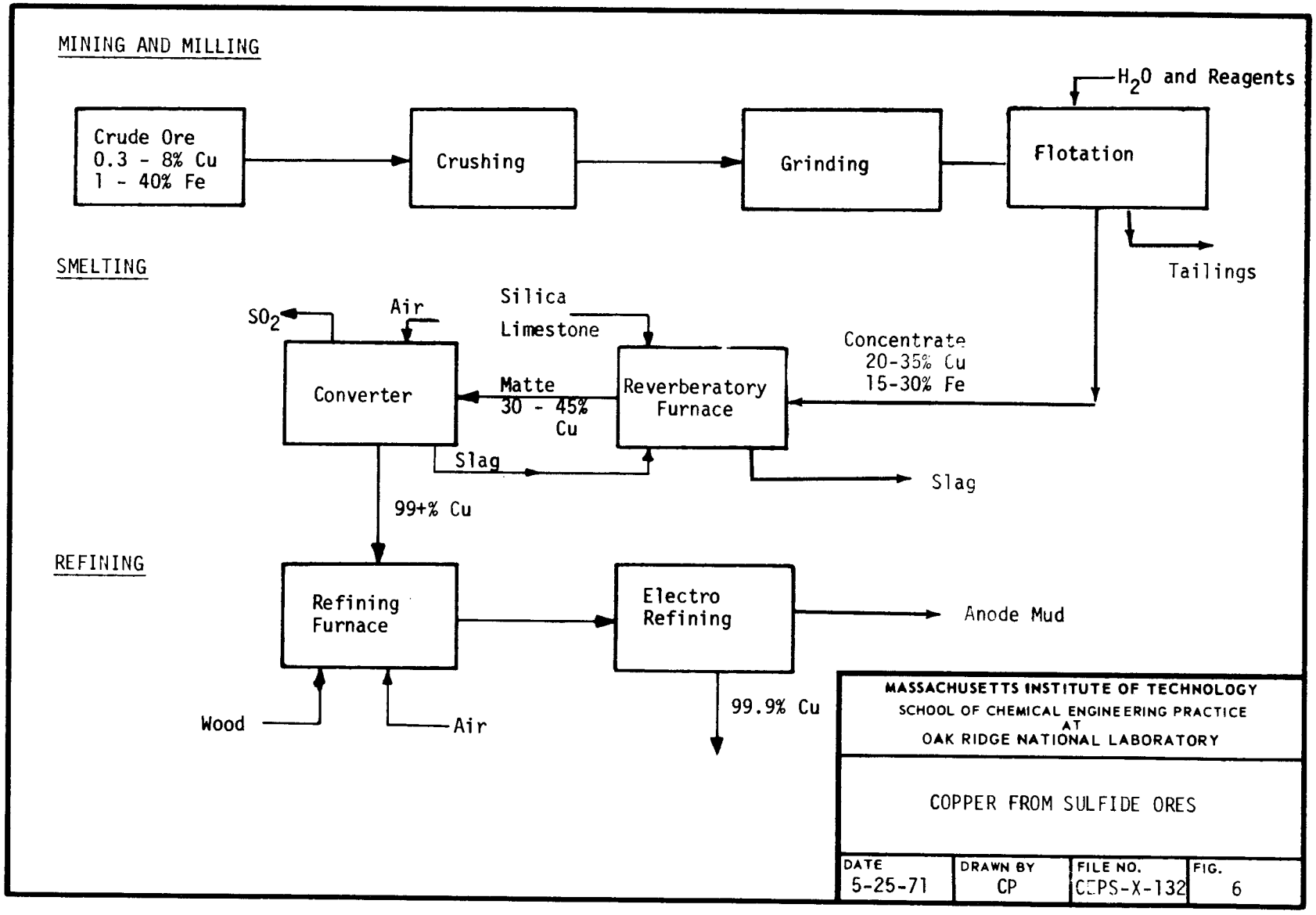
FILE NO.
CEPS-X-132
FIG.
5


MINING AND MILLING
H_2O and Reagents
Crude Ore
0.3 - 8% Cu
1 - 40% Fe
Crushing
Grinding
Flotation
Tailings
SMELTING
SO_2
Air
Silica
Limestone
Converter
Matte
30 - 45%
Cu
Reverberatory
Furnace
Concentrate
20-35% Cu
15-30% Fe
Slag
Slag
99+% Cu
REFINING
Refining
Furnace
Electro
Refining
Anode Mud
Wood
Air
99.9% Cu
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY
COPPER FROM SULFIDE ORES
DATE
5-25-71
DRAWN BY
CP
FILE NO.
CEPS-X-132
FIG.
6

excess oxygen. The cast anodes and pure copper cathodes are then suspended in an electrolyte of copper sulfate and sulfuric acid for electrolysis. When a voltage is applied, copper is dissolved from the impure anode and is plated out of solution on the cathode. Typical operating conditions are 0.15 v and a 15 amp/ft^2 current density. During the refining process impurities such as gold, selenium, silver, and tellurium fall to the bottom of the tank as anode mud. This anode mud may further be processed for the recovery of valuable by-product metals.

7.2 Energy Requirements for Copper Production from Virgin Ores

The main energy consuming steps in the overall process are outlined below and summarized in Table 9. Detailed calculations are shown in Appendix 12.4.

1. Mining and Milling. The mining, crushing, grinding, and froth flotation all consume 4296 kwh per ton of Cu produced from a 1% ore. Of this energy 19% is used for crushing, 53% for grinding, 12% for ore flotation, and the rest for miscellaneous plant use. The total mining and milling energy per ton of Cu product is inversely proportional to the copper concentration in the ore (C-1, C-16) for a given type of sulfide porphyry ore. Since lime is used to control the pH in the flotation step, the energy equivalent for the preparation from limestone calcination and grinding is also included.

2. Smelting. The primary consumption of energy is to fuel the reverberatory furnace. Either pulverized coal, gas, or fuel oil is used to supply 7911 kwh/ton Cu thermal energy, the single most energy intensive step in the entire process. The energy equivalent for preparing the fluxes, limestone and silica,must also be added to this total, 48 kwh/ton Cu.

3. Refining. Natural gas is used in the refining furnace for heating. The electrical energy consumption for the electrolysis is 200 kwh/ton of Cu compared to the natural gas requirement of 1025 kwh/ton in the refining furnace.

The equivalent coal energy consumption for refining a 1% Cu sulfide ore is 13,532 kwh/ton Cu compared to 24,759 kwh/ton for a 0.3% ore. An increase of nearly 75% due to the increased mining and milling requirements.

7.3 Recovery of By-Products in Copper Processing

By-products in copper production are recovered in two processing steps: (1) smelting, the liberated SO_2 is recovered as H_2SO_4 and (2) electrorefining, the gold, silver, tellurium and selenium can be purified from the anode mud. The extraction and recovery of the iron sponge from the reverberatory furnace has been shown to be economically unfeasible (C-17). In the five-year period 1959-63, approximately 32% of United States gold production and

Table 9. Energy Expenditure Associated with the Production of Copper from Virgin Sulfide Ores

Basis: 1 ton of Copper, Gibb's Free Energy Change = 718.2 kwh

	Energy Requirements (kwh)		Equivalent Coal Energy Requirements kwh	
	1% Ore	0.3% Ore	1% Ore	0.3% Ore
Mining and Milling				
Crushing, Grinding, Flotation, Miscellaneous	4296	14,320	4296	14,320
Flotation Reagent Energy Equivalent	488+13(E)	1627+39(E)	521	1,725
Smelting				
Smelting Furnace	7032+15(E)	7032+15(E)	7070	7,070
Silicate Consumption Energy Equivalent	38(E)	38(E)	95	95
Limestone Consumption Energy Equivalent	10(E)	10(E)	25	25
Refining				
Refining Furnace	1025	1025	1025	1,025
Electrolysis	200(E)	200(E)	500	500
Total	12,841 + 276(E)	24,004 + 302(E)	13,532	24,759

(E) = electrical energy

28% of the silver production were derived from processing of copper ores. U.S. copper ores contain very little cobalt and molybdenum, but are fairly rich in selenium and tellurium. The copper ores in the Belgian Congo, however, supply 53% of the world's cobalt production. In 1963 0.4 million tons of sulfuric acid were produced as a by-product in several copper plants using the sulfide ores.

7.3.1 Recovery of Sulfuric Acid from Converter Gases

The off gases from the converter are rich in sulphur dioxide (SO_2) and are recovered for sulfuric acid production. For typical U.S. grade copper ores, approximately 1.25 tons of H_2SO_4 (98-100%) are produced per ton of copper (C-15). The SO_2 is catalytically oxidized to SO_3 in a converter at 500°C and high pressures. The SO_3 is then absorbed in a dilute H_2SO_4 solution. The energy requirements for the process are chiefly electrical power for the compressors and associated equipment. For a 300 ton/day 98% H_2SO_4 plant with a 2500-HP blower, the additional energy requirement is 150 kwh/ton of sulfuric acid produced.

7.3.2 Recovery of Gold, Silver, Selenium, and Tellurium

The anode mud from the electrorefining of crude copper is processed for the recovery of the valuable metals as shown schematically in Fig. 7. The anode mud is first leached with sulfuric acid to reclaim the residual copper. The product is then smelted resulting in two distinct molten slags: a liquid mixture of gold and silver and a lighter slag containing selenium and tellurium. The gold and silver are isolated from the mixture by electrolysis, silver is deposited on the cathode, while the gold is retained on the diaphragm separating the anode from the cathode. The selenium and tellurium in the other liquid fraction are isolated by selective precipitation (acidification and neutralization using SO_2 and soda ash).

For every ton of anode mud, 9.38 lb of gold, 412.5 lb of silver, 30 lb of tellurium, and 150 lb of selenium are commonly recovered (C-11). The anode mud produced per ton of copper during the refining step depends largely on the type of ore and the beneficiation of the ore; however, typically 14.5 lb of mud are generated for every ton of copper.

The smelting of the anode mud and the gold-silver electrolysis are the two most energy intensive steps of the whole by-product recovery. The total additional energy requirements for the recovery of these four metals starting from anode mud areshown in Table 10. The detailed calculation can be found in Appendix 12.4. It should be pointed out that the energy requirements shown in this table are based on the production of each metal separately. The total energy consumption for processing one ton of anode mud is 5550 kwh. Since approximately 0.00725 ton of mud is produced per ton of copper, the additional total energy requirements based on a ton of copper are 40.23 kwh.

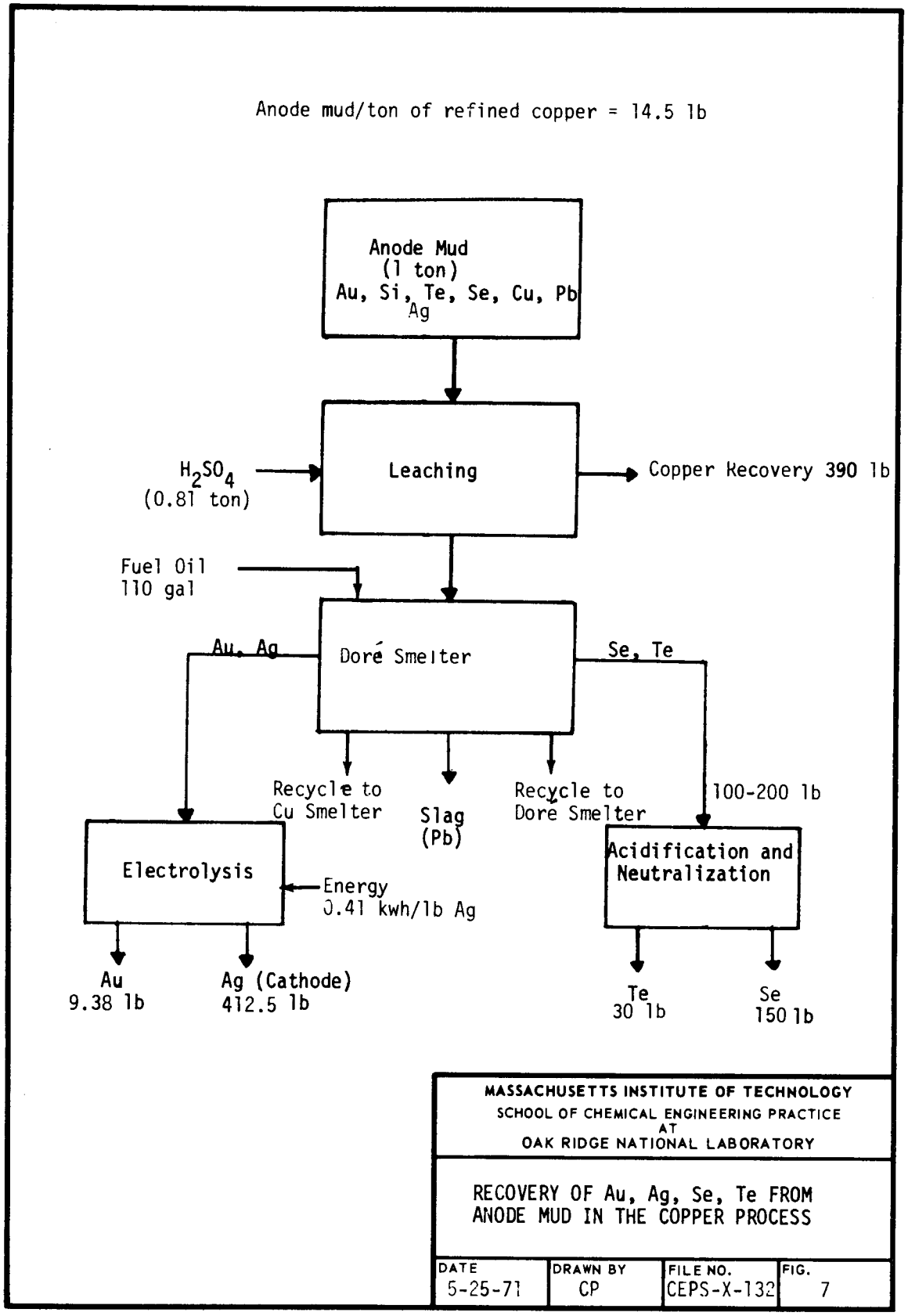

Anode mud/ton of refined copper = 14.5 lb
Anode Mud
(1 ton)
Au, Si, Te, Se, Cu, Pb
Ag
H_2SO_4
(0.81 ton)
Leaching
Copper Recovery 390 lb
Fuel Oil
110 gal
Au, Ag
Doré Smelter
Se, Te
Recycle to
Cu Smelter
Slag
(Pb)
Recycle to
Doré Smelter
100-200 lb
Electrolysis
Energy
0.41 kwh/lb Ag
Acidification and
Neutralization
Au
9.38 lb
Ag (Cathode)
412.5 lb
Te
30 lb
Se
150 lb
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY
RECOVERY OF Au, Ag, Se, Te FROM
ANODE MUD IN THE COPPER PROCESS
DATE
5-25-71
DRAWN BY
CP
FILE NO.
CEPS-X-132
FIG.
7

Table 10. Additional Energy Requirements to Recover Copper By-Products

Material	Lb Produced Per ton Cu	Total Energy kwh/ton Product	Equivalent Coal Energy kwh/ton Product	Equivalent Coal Energy kwh/ton Cu
A. Ref. (C-11)				
Sulfuric Acid	2500	150	375	469
Gold	0.068	1.02×10^6	1.12×10^6	38
Silver	2.99	2.33×10^4	2.54×10^4	38
Selenium	1.09	6.24×10^4	6.59×10^4	35.8
Tellurium	0.22	3.14×10^5	3.33×10^5	36.3
B. Ref. (C-2)				
Gold	0.091	1.17×10^6	1.24×10^6	56.5
Silver	2.95	3.61×10^4	3.82×10^4	56.5
Selenium	0.49	5.20×10^5	0.99×10^6	244
Tellurium	0.23	9.21×10^5	1.64×10^6	191

All the above figures are based on operating data obtained from the American Smelting and Refining Co. (C-11). The energy consumption as well as the by-product recovery is governed to a fairly large extent by the type of copper ore and details of process operation. In the second half of Table 10, production statistics as obtained from the United States Metals Refining Co. (C-2) are shown and some variance in the different quantities is apparent. While the gold and silver production agrees fairly well, there is a substantial difference for the selenium and tellurium. This difference can be attributed to the source of the virgin copper ore and the degree of purification of the final products, selenium and tellurium. Other manufacturers employ a somewhat different process scheme, but the methods of separation are the same (C-18).

7.4 Recycle of Copper from Metal Scrap

An important copper reserve is the ever-increasing amount of recyclable copper which can provide about one-third of the nation's requirements (C-16). There are no statistical data detailing the amount of copper consumed in dissipative uses. However, if it is assumed that three-fourths of the new copper is consumed in the manufacture of reclaimable products, it is estimated that this secondary copper supply constitutes a 35 million ton copper reserve.

Figure 8 is a schematic flowsheet for copper recovery from scrap metal. The recycling process depends primarily on the level of impurities associated with the scrap. If the scrap metal is more than 98% pure copper, a single smelting stage is sufficient, otherwise a pretreatment step is necessary. Non-metallic contaminants like wire insulation, etc., are removed by burning, followed by smelting at 2000°F. Coke is added as an oxygen scavenger, while limestone and soda ash are used to flux the arsenic and lead. An electrorefining step, identical to virgin ore processing, is the last step in the process.

For 98% copper scrap, the energy requirements consist of heating the charge to a melt, 236(E) kwh/ton of recovered copper (see Appendix 12.4 for calculations). For other scrap smelting, flux preparation and electrorefining contribute to the energy consumption. Table 11 shows the energy requirements for each step along with an equivalent coal energy. The total energy for recycle is 1258 kwh/ton Cu or an equivalent coal energy of 1559 kwh/ton Cu. Power costs for both the production from virgin ores and recycle scrap are indicated for comparison.

The energy requirements for the production of copper from virgin ores will increase in the future as poorer grade sulfide ores are utilized. The energy requirements for recycle of copper are less than 7% of those for processing from virgin ores.

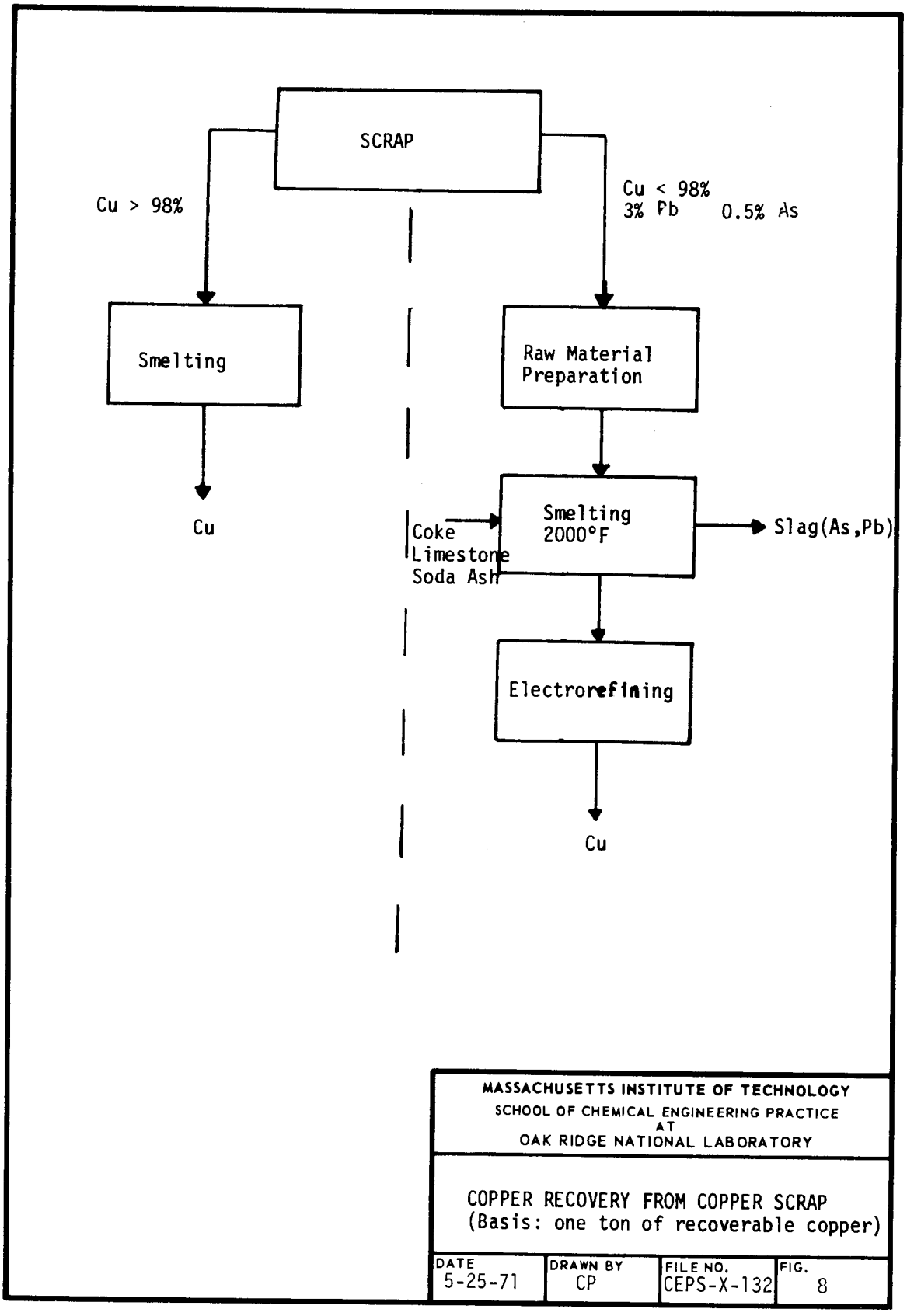

SCRAP
Cu > 98%
Cu < 98%
3% Pb
0.5% As
Smelting
Cu
Raw Material Preparation
Smelting 2000°F
Coke
Limestone
Soda Ash
Slag(As,Pb)
Electrorefining
Cu
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY
COPPER RECOVERY FROM COPPER SCRAP
(Basis: one ton of recoverable copper)
DATE 5-25-71
DRAWN BY CP
FILE NO. CEPS-X-132
FIG. 8

Table 11. Energy Requirements and Power Costs for the Production of Copper from Virgin Ores and from Recycle Scrap

Basis: 1 ton of pure Cu, Sales Price = $1200

	Total Energy (kwh)	Equivalent Coal Energy (kwh)	Power Costs ($)
Virgin Ores			
1. Processing 1.0% Cu	12,841+276(E)	13,532	14.22
2. Processing 0.3% Ore	24,004+302(E)	24,759	25.51
Recycle			
1. 98% Cu Scrap	236(E)	590	1.18
2. Impure Scrap			
a) Pretreatment	1025	1025	0.85
b) Energy equivalent for Coke, Limestone, and Soda Ash	35	35	0.04
c) Refining	200(E)	500	1.00
	1,058 + 200(E)	1,559	1.89

8. TITANIUM (Ti)

Titanium is the fourth most abundant metallic element in the earth's crust and ninth most common element (0.4% abundance). It is a silvery-gray, paramagnetic metal having strengths equal or superior to steel, although it has approximately half the density of alloy steel. At present, approximately 95% of the Ti sponge metal produced is used in aircraft and aerospace components. Production of the metal in the United States has been doubling every seven years, and projections for 1983 are 50,000 to 70,000 tons/year (T-14). Although Ti is abundant, the major minerals, rutile (TiO_2) and ilmenite ($FeTiO_3$), have limited resources. Moreover, since 90% of all the Ti produced is used dissipatively as pigments and there is an insignificant recycle of Ti metal scrap, a serious shortage of high grade ores is expected by the early 1980's.

Alternate sources of Ti are generally very dilute and contain numerous other metallic elements which make the extraction process difficult. In this study the following six ores were evaluated:

1. Beach sands and dune sand deposits high in rutile (∿24% rutile)
2. Beach sands containing ilmenite (∿1.3% TiO_2 equivalent)
3. Ilmenite rock deposits (10-20% TiO_2 equivalent)
4. Ferruginous ilmenite rock deposits (10-30% TiO_2 equivalent)
5. High alumina clays from the Bayer bauxite process (∿5% TiO_2 equivalent)
6. Titanium bearing soil (∿0.2-1.5% TiO_2 equivalent).

For each ore the energy requirements for mining, beneficiation, and chemical processing have been estimated on the basis of one ton of Ti metal product.

8.1 Production of Titanium Metal from Virgin Ores

Titanium metal is currently manufactured by the Kroll Process in which rutile (∿95% TiO_2) or an enriched ilmenite slag (∿90% TiO_2 equivalent) is chlorinated to titanium tetrachloride, followed by reduction with magnesium to form Ti sponge. The energy requirements in chemical processing for the six ores are the same; the differences arise in the mining and beneficiation prior to the Kroll process.

Although rutile (∿95% TiO_2) is the purest ore, the resources are limited; considerable effort has been expended on the development of processes for beneficiating ilmenite and ferruginous ilmenite. Ilmenite concentrates (<53% TiO_2) presently are used exclusively in the manufacture of pigments. The high iron content in the ilmenite results in significant $FeCl_3$ losses in the

Kroll Process (T-6, 9, 14). One of the promising new methods for upgrading the ilmenite for suitable Kroll processing is the smelting with carbon in an electric furnace at 3000°F.

$$FeTiO_3 + C \longrightarrow Fe + TiO_2 + CO$$

The Japanese titanium industry (T-10) has successfully commercialized this process to produce ilmenite slags containing 90% TiO_2. In this study energy calculations have been made on the assumption that smelting 40-50% equivalent TiO_2 ilmenite concentrates to produce ilmenite slags of 90% TiO_2 will become standard practice (T-6, 14). The molten iron which is tapped from the smelting furnace can be charged to basic oxygen furnaces to produce steel.

The mining and beneficiation of the six different ores differ slightly in detail; however, the basic unit operations are nearly identical. For the sake of brevity, only one ore beneficiation will be described in this section, and the reader is referred to Appendix 12.5.2 for further details. Figure 9 is a schematic flow diagram for the recovery of ilmenite slag and the simultaneous recovery of zirconium and pig iron from beach sands. Low grade beach sand deposits averaging 1-2% TiO_2 can be recovered by dredging and pumping the material as a slurry to the beneficiating plant (T-3). From a 1.4% ore 29,000 tons of solids are mined to recover 300 tons of 90% ilmenite. The more important concentration steps are:

1. Gravity concentration and washing

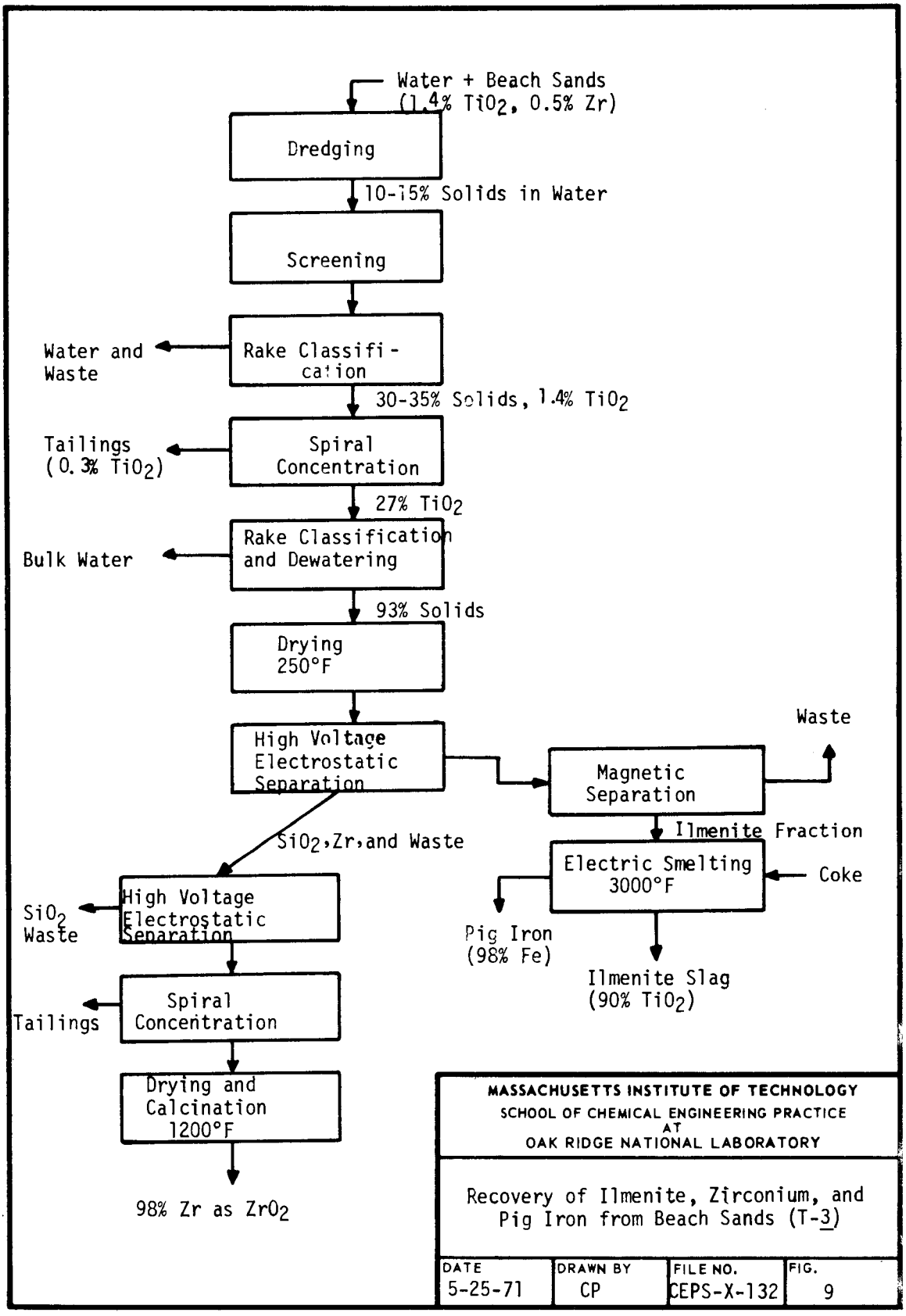
2. High voltage electrostatic separation (40,000 v, 15 mA) (silicate minerals, quartz, zirconium)

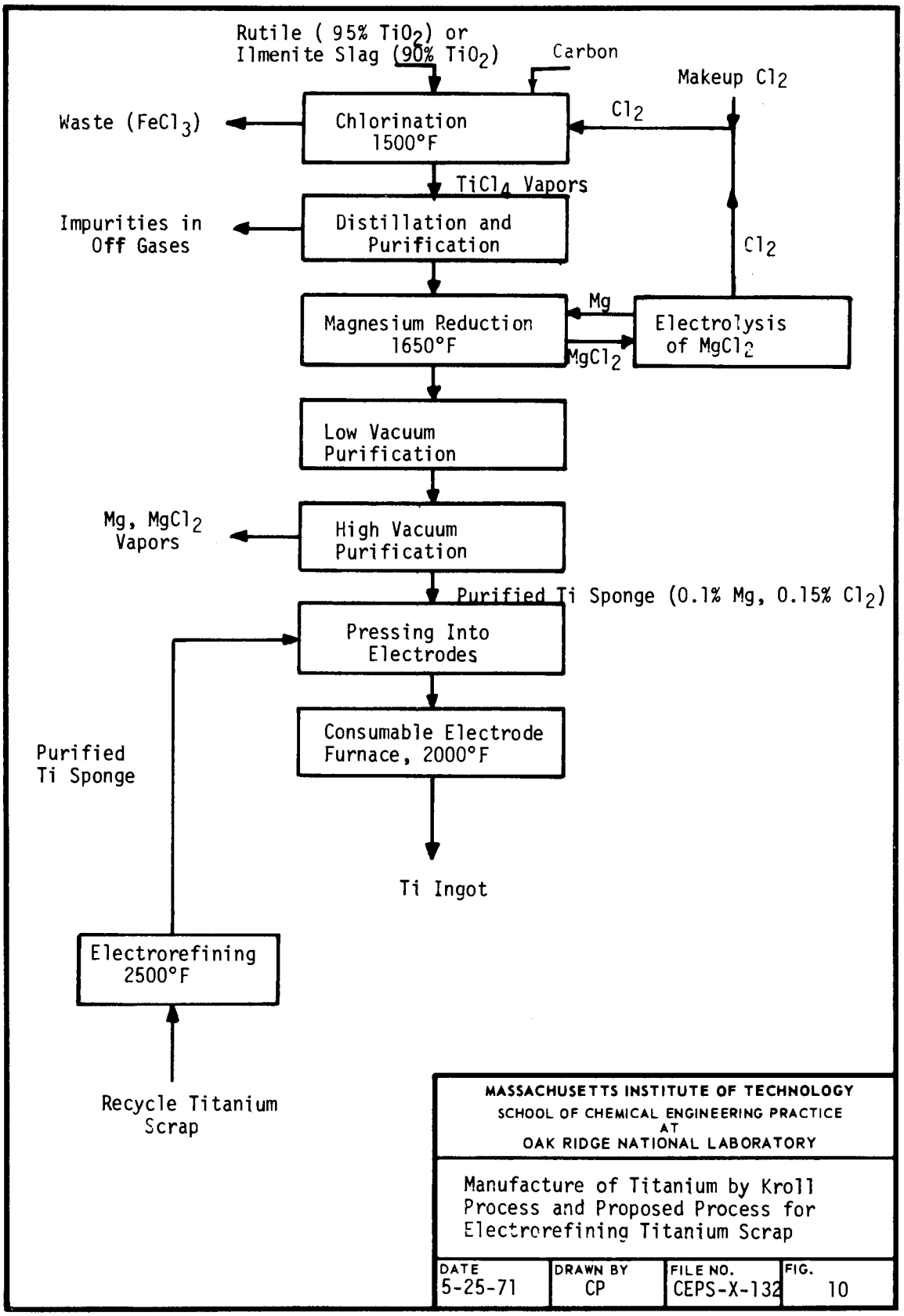
3. Magnetic separation and smelting.

The beneficiated rutile or ilmenite slag containing 90% or greater equivalent TiO_2 is used as the starting point for the Kroll Process depicted schematically in Fig. 10. Table 12 shows the raw material requirements of the process for one ton of Ti produced, starting from either rutile or ilmenite slag. The main energy consuming steps in the process can be conveniently divided into six categories.

Table 12. Material Requirements for Making One Ton of Titanium Metal by Kroll Process (T-6, 14)

Raw Materials	Feed Material (tons)	
	Rutile	Ilmenite Slag (90% TiO_2)
Ore	2.0	2.5
Chlorine	1.0	1.5-1.7
Magnesium	0.1-0.2	0.1-0.2
Carbon	1.0	1.0


Water + Beach Sands
(1.4% TiO_2, 0.5% Zr)
Dredging
10-15% Solids in Water
Screening
Water and Waste
Rake Classification
30-35% Solids, 1.4% TiO_2
Tailings (0.3% TiO_2)
Spiral Concentration
27% TiO_2
Bulk Water
Rake Classification and Dewatering
93% Solids
Drying 250°F
High Voltage Electrostatic Separation
Waste
Magnetic Separation
Ilmenite Fraction
SiO_2, Zr, and Waste
Electric Smelting 3000°F
Coke
SiO_2 Waste
High Voltage Electrostatic Separation
Pig Iron (98% Fe)
Ilmenite Slag (90% TiO_2)
Tailings
Spiral Concentration
Drying and Calcination 1200°F
98% Zr as ZrO_2
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY
Recovery of Ilmenite, Zirconium, and Pig Iron from Beach Sands (T-3)
DATE 5-25-71
DRAWN BY CP
FILE NO. CEPS-X-132
FIG. 9


Rutile (95% TiO_2) or
Ilmenite Slag (90% TiO_2)
Carbon
Makeup Cl_2
Waste ($FeCl_3$)
Chlorination
1500°F
Cl_2
$TiCl_4$ Vapors
Impurities in
Off Gases
Distillation and
Purification
Cl_2
Mg
Magnesium Reduction
1650°F
Electrolysis
of $MgCl_2$
$MgCl_2$
Low Vacuum
Purification
Mg, $MgCl_2$
Vapors
High Vacuum
Purification
Purified Ti Sponge (0.1% Mg, 0.15% Cl_2)
Pressing Into
Electrodes
Consumable Electrode
Furnace, 2000°F
Purified
Ti Sponge
Ti Ingot
Electrorefining
2500°F
Recycle Titanium
Scrap
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY
Manufacture of Titanium by Kroll
Process and Proposed Process for
Electrorefining Titanium Scrap
DATE
5-25-71
DRAWN BY
CP
FILE NO.
CEPS-X-132
FIG.
10

1. Chlorination of the Slag. A mixture of rutile or ilmenite slag and finely divided carbon is fluidized with chlorine gas at 1500°F. The main reactions are:

Rutile:

$$TiO_2(s) + 2C(s) + 2Cl_2(g) \rightarrow TiCl_4 + 2CO(g)$$

Ilmenite:

$$FeTiO_3(s) + \frac{3}{2}C(s) + \frac{7}{2}Cl_2(g) \rightarrow TiCl_4(s) + FeCl_3(s) + \frac{3}{2}CO_2(g)$$

After the reaction temperature has been obtained, both reactions are exothermic and self sustaining. Chlorine losses with ilmenite slags are 1.5 to 1.7 tons/ton Ti compared to about one ton/ton Ti with the rutile (T-6, 13, 14)

2. $TiCl_4$ Purification. The $TiCl_4$ from the chlorinator is purified with hydrogen sulfide and condensed to remove the iron, vanadium, Cl_2, CO, CO_2, and other gaseous impurities. The crude $TiCl_4$ is then distilled overhead to free it from $FeCl_3$ and other trace contaminants which adversely affect the properties of the final titanium product.

3. Magnesium Reduction. Purified liquid $TiCl_4$ is slowly introduced into a tightly sealed reaction vessel (T-3, 8, 9, 14) (placed in an oil or gas fired furnace) containing liquid magnesium metal under a positive pressure of pure helium gas. The reaction is highly exothermic.

$$TiCl_4(\ell) + 2Mg(\ell) \xrightarrow{1550°F} Ti(s) + 2MgCl_2(\ell)$$

$$\Delta H° = -2700 \text{ kwh/ton Ti}$$

By-product $MgCl_2$ is tapped at suitable intervals. The furnace is not heated during the addition of $TiCl_4$, but at the end of the reaction, heating is continued for perhaps an hour. The reaction pot is removed from the furnace and allowed to cool to room temperature before opening in a dry room, humidity at a dew point of at least -40°C.

4. Purification of Ti Sponge. Since the Ti sponge from the Kroll reactor contains considerable $MgCl_2$ and a small amount of magnesium metal, it is heated in an electric furnace under a vacuum of 10-50 μ pressure at 1650-1700°F to distill off the impurities (T-1, 8). To reduce the magnesium level to 0.10% and the chloride to 0.15%, government specifications (T-14), the distillation must be continued for several hours.

5. Melting Ti Sponge to Form Ingot. Purified Ti sponge is pressed into rectangular electrode sections which are then welded and consumed (melted) in an electric arc furnace (under vacuum) to form ingots (T-14). A second remelt is usually employed to attain homogeneity in the finished product.

6. Electrolysis of $MgCl_2$. The electrolysis of the $MgCl_2$ tapped from the reduction reactor is the most energy consuming step of Ti production. The net consumption of magnesium in the process is about 0.1 ton/ton product.

8.2 Energy Requirements for Ti Production

Equivalent coal energy requirements for the production of Ti metal are shown in Table 13 to vary from 126,280 kwh/ton Ti for high grade rutile to 206,750 kwh/ton for soil deposits. It can be seen that the production of Ti is heavily dependent on electricity, 55% of total energy requirements.

The energy requirements for beneficiation reflect the concentration of the titanium mineral in the ores and the mineralogical nature of the deposit. For example, per ton of Ti, the energy requirements for crushing a 20% TiO_2 rock ore and a 1.4% TiO_2 beach sand are nearly equal (Table 13). The relative difficulty of beneficiating low grade soil deposits containing 0.2% TiO_2 is reflected in the large energy requirement, 24,300 kwh of electricity and 2500 kwh of coal per ton of titanium metal produced.

For all other ores except common soil, smelting is the most energy consuming step of the beneficiation, varying from 5200 to 6500 kwh/ton Ti depending on the amount of iron impurities (T-4, 14). In the case of ferruginous ilmenites which cannot be concentrated by mechanical means, more severe smelting procedures are necessary, and the energy consumed is close to 6900 kwh/ton of Ti.

The electrolysis of $MgCl_2$ is the single most energy consuming step in the whole process. Process improvements aimed at reducing Mg and Cl_2 losses and efficient utilization of the heat generated in the chlorination and subsequent reduction steps will result in substantial energy savings.

Included in Table 13 is the Gibbs Free Energy of formation for Ti production (3220 kwh/ton). This is the minimum theoretical energy necessary for the recovery of Ti from TiO_2 by the overall reaction

$$TiO_2 + 2C \rightarrow Ti + 2CO$$

Table 13. Energy Requirements for the Production of Titanium Metal (Ingots) from Several Ores
(Basis: 1 ton Ti)

Gibbs Free Energy Change = 3200 kwh; Sales Price = $3200

Raw Material	Rutile (98% TiO_2)	Ilmenite Slag (90% TiO_2)	Ilmenite Slag (90% TiO_2)	Ilmenite Slag (90% TiO_2)	Ilmenite Slag (90% TiO_2)	Ilmenite Slag (90% TiO_2)
Occurrence	Beach Sands (24% TiO_2)	Beach Sands (1.4% TiO_2)	Rocks (20% TiO_2)	Ferruginous Rocks (35% TiO_2)	High Alumina Clay (~5% TiO_2)	Soil (0.2% TiO_2)
	(kwh)	(kwh)	(kwh)	(kwh)	(kwh)	(kwh)
1. Mining and Beneficiation						
Drilling, Dredging, Blasting, and Stripping	56(E)	410(E)	20(E)	15(E)	155(E)	3680(E)
Crushing and Grinding	60(E)	120(E)	125(E)	80(E)	220(E)	5300(E)
Gravity Concentration (Including Flotation and Drying)	18(E)	190(E)	25(E)	-	200(E)	1720(E)
Magnetic Concentration	16(E)	140(E)	15(E)	-	55(E)	1300(E)
High Intensity Electrostatic and/or Magnetic Separation	40(E)	550(E)	34(E)	-	190(E)	4500(E)
Roasting	-	-	-	-	2100	2500
Miscellaneous (Tailings Disposal, Pumping, etc.)	40(E)	320(E)	27(E)	-	270(E)	4300(E)
Smelting of Slag (90% TiO_2)	-	5200(E)	5400(E)	6900(E)	6500(E)	6500(E)
Total	230(E)	6930(E)	5646(E)	6995(E)	7590(E) + 2100	27,300(E) + 2500
2. Processes						
Chlorination	600(E)	1000(E)	1000(E)	1000(E)	1000(E)	1000(E)
$TiCl_4$ Purification	2000(E)	2200(E)	2200(E)	2200(E)	2200(E)	2200(E)
Mg Reduction Reactors	9200	9200	9200	9200	9200	9200
Fuel for Dry Room	11,500	11,500	11,500	11,500	11,500	11,500
Ti Sponge Purification	5000(E)	6500(E)	6500(E)	6500(E)	6500(E)	6500(E)
Electrolysis of $MgCl_2$	16,500(E)	16,500(E)	16,500(E)	16,500(E)	16,500(E)	16,500(E)
Equivalent of Materials Consumed (Mg, Cl_2, and C)	3,500(E) + 19,100	5,200(E) + 19,900	5,200(E) + 19,900	5,200(E) + 19,900	5,200(E) + 19,900	5,200(E) + 19,900
Consumable Electrode Furnace	5600(E)	5600(E)	5600(E)	5600(E)	5600(E)	5600(E)
Miscellaneous (Heating, Inert Gases)	2900	2900	2900	2900	2900	2900
Total	33,200(E) + 42,700	37,000(E) + 43,500	37,000(E) + 43,500	37,000(E) + 43,500	37,000(E) + 43,500	37,000(E) + 43,500
3. Totals for (1) and (2)	33,430(E) + 42,700	43,930(E) + 43,500	42,646(E) + 43,500	43,995(E) + 43,500	44,590(E) + 45,600	64,300(E) + 46,000
Equivalent Coal Energy	126,275	153,325	150,115	153,488	157,075	206,750

(E) = electrical energy

8.3 Recovery of Co-Products and By-Products

1. Zirconium (Co-Product). Beach sands containing ilmenite have 0.05 to 1% of zirconium which can be recovered from the tailings of an ilmenite beneficiation plant (T-3). Figure 9 is a flowsheet for one typical process, wherein 98% pure zirconium metal as ZrO_2 is recovered. Additional processing steps for zirconium involve a high voltage electrostatic precipitation followed by spiral concentration and drying at 1200°F to remove organics adsorbed on the surface of the zirconia particles.

Typically 30 lb of zirconia can be recovered per 100 lb of ilmenite slag or per 40 lb of Ti metal. The additional energy requirement for this recovery is approximately 400-650 kwh/ton Ti, or 530 to 870 kwh/ton of zirconia.

2. Pig Iron (By-Product). Pig iron (98-99% Fe) is a by-product of the smelting operation for concentrating ilmenite (T-4, 7). The additional energy consumption in producing pure pig iron suitable for use in the steel furnace depends on the level and type of impurities from the smelting operation. Remelting in an electric furnace with the addition of fluxes such as limestone is usually sufficient to purify by-product pig iron (T-7). Approximately 0.7 ton pig iron can be obtained per ton of ilmenite slag or 0.4 ton titanium. The energy expenditure for the additional purification is estimated to be 3000 to 5000 kwh/ton Ti or 1710-2860 kwh/ton pig iron.

3. Monazites, Euxenites, and Other Rare Elements. Rutile and ilmenite sands often contain varying amounts of monazite, garnet, euxenite and columbite depending on the geographic location of the deposit. In some cases they may also contain some rare earths like thorium, uranium, and tantalum, and then the recovery of Ti takes on a secondary importance (T-9, 13). The energy for the recovery of these rare earths and special minerals has not been evaluated in this study.

8.4 Recycle of Titanium from Scrap Metal

Approximately 90% of all the titanium consumed is used dissipatively as pigments, and the major fraction of the remainder is employed in the aircraft and missile industry. At present recycle of Ti from scrap metal is negligible.

Titanium scrap can be divided into two categories: "home scrap" and "consumer scrap." To produce the high purity Ti used in the aircraft industry, often 6-8 lb of metal (crude Ti) have to be discarded per lb of finished product. The excess material, referred to as home scrap, can be recycled with Ti sponge (up to 40% scrap and 60% new Ti) and purified in electric arc furnaces. Typical operating data from the industry show that approximately 45% of the total home scrap is used in this way (T-14), the remainder being stockpiled as inventory. Consumer scrap on the other hand comes primarily from titanium alloys requiring extensive purification before being recycled.

The increasing home and consumer scrap inventory might be economically electrorefined in a fused salt bath for recycle. This method has been demonstrated by the U.S. Bureau of Mines on a pilot plant scale (T-5). The electrorefined sponge can then be formed into ingots in an electric arc furnace. Electrical energy consumption for the electrorefining cell (10,000 amp) is approximately 10,000 kwh/ton of titanium refined. Overall energy consumption for recycle is estimated at 15,600 kwh(E)/ton Ti, or an equivalent coal energy of 39,000 kwh/ton Ti, or 25 to 29% of the energy requirements for Ti production from rutile and ilmenite, respectively. The cost of total energy requirements for Ti production from two typical virgin ores is compared to that for recycle in Table 14.

Table 14. Energy Costs for the Production of Titanium from Virgin Ores and Recycle Metal Scrap

Basis: 1 ton of Ti Metal

Raw Material	Rutile ($)	Ilmenite Slag (90% TiO_2 Equivalent) from Beach Sands ($)	Recycle Metal Scrap ($)
Ore Beneficiation			
Electrical Energy	1.15	34.65	-
Thermal Energy	-	-	-
Chemical Processing			
Electrical Energy	166.	185.	-
Thermal Energy	42.7	43.5	-
Electrorefining (only for scrap)			78
Total	$ 209.85	$ 263.15	$ 78

9. CONCLUSIONS

Table 15 summarizes the energy requirements for the production of magnesium, aluminum, iron, copper, and titanium metals from their virgin ores and the energy for recycle of copper and titanium from scrap metal. The energy requirements for Mg production will stay essentially constant (~90,930 kwh/ton) in the future because of its infinite resource in sea water. As poorer grade bauxite (~30% Al_2O_3) ores are used in the future,

Table 15. Summary of the Energy Requirements for the Production and Recycle of Metals

Metal	Main Source	Equivalent Coal Energy (kwh/ton)
Magnesium	Sea Water	90,930
Aluminum	Bauxite 50% Alumina	51,470
	Bauxite 30% Alumina	59,540
	Clays	65,970
	Anorthosite	72,360
Iron	High Grade Hematite	3,180
	Magnetic Taconite	3,560
	Specular Hematite	4,050
	Non-magnetic Taconites	4,140
	Iron Laterites	5,180
Copper	1% Sulfide Ore	13,530
	0.3% Sulfide Ore	24,760
	98% Scrap Recycle	590
	Impure Cu Scrap Recycle	1,560
Titanium	High Grade Rutile Ore	126,280
	Ilmenite Rocks	150,120
	Ilmenite Beach Sands	153,330
	Ferruginous Rocks	153,490
	High Alumina Clays	157,080
	High Ti Soils	206,750
	Ti Scrap Metal Recycle	39,000

energy requirements for Al production will increase only 16% (51,470 - 59,540 kwh/ton). However, eventual use of high alumina clays and anorthosite deposits will increase the energy consumption by 30 and 40%, respectively. For iron production use of magnetic taconites will increase the energy requirements 12% compared to the high grade hematite ores (now essentially exhausted). Although taconite reserves in the United States are very large, eventual use of other iron ores like specular hematites, non-magnetic taconites, and iron laterites will result in higher energy requirements (4000 - 5200 kwh/ton). Use of low grade copper ores (0.3%) will adversely effect the energy requirements by as much as 75%. High grade rutile ores for Ti production have very small reserves, and use of other minerals containing ilmenite will result in a 20% increase in the energy requirements. Ultimate use of titanium bearing soils will yield a 72% increase in energy consumption over that for rutile ore.

Energy requirements for the recycle of copper from 98% Cu scrap metal is only 590 kwh/ton compared to 13,530 kwh/ton for virgin ore processing. Recycle of scrap containing impurities like lead and arsenic requires 1560 kwh/ton. Presently about 19% of the total copper production is recycled; potentially, 75% of the copper can be recycled. Recycle of titanium metal is minimal (<1%) since 90% of the uses are dissipative. Approximately 39,000 kwh/ton of Ti are necessary for the recovery of Ti from scrap metal.

By-products which can be potentially recovered from Cu ores include sulfuric acid, gold, silver, tellurium, and selenium. Zirconium and pig iron are the principal by-products in the processing of titanium. Energy requirements per ton of by-product and per ton of copper or titanium are summarized in Table 16.

Table 16. Additional Energy Requirements for Recovery of By-Products from Cu and Ti Processing

By-Products	Equivalent Coal Energy/Ton	
	kwh/ton By-product	kwh/ton Cu or Ti
Copper		
H_2SO_4	375	469
Gold	1.12×10^6	38
Silver	2.54×10^6	38
Tellurium	6.59×10^4	35.8
Selenium	3.33×10^5	36.3
Titanium		
Zirconium	530 - 870	400 - 650
Pig Iron	1710 - 2860	3000 - 5000

10. RECOMMENDATIONS

The energy requirements evaluated in this study are based on (where possible) present technology and existing industrial flowsheets. For those ores not currently used, the energy needs were estimated based on process information or theoretical studies available in the literature. If important developments in ore beneficiation or chemical reduction are made, the corresponding energy requirements will have to be re-evaluated.

11. ACKNOWLEDGEMENT

We would like to thank our consultants, W. Fulkerson and H.E. Goeller, for their assistance in this project.

12. APPENDIX

12.1 Magnesium

12.1.1 Energy Requirements for Magnesium Production

The specific energies involved in Mg production from sea water by the Dow Electrolytic Process are given below.

1. Sea Water Pretreatment. Per ton of Mg, 181,600 gal of water must be pumped to the processing plant. A total pressure drop of 600 ft of water has been assumed for pumping sea water from the ocean through the various unit operation steps (thickeners, filters, etc.). An 85% pump efficiency has been assumed; therefore, the pumping energy is

$$181{,}600 \text{ gal}\left(\frac{3.785 \text{ kg/gal}}{0.453 \text{ kg/lb}}\right)(600 \text{ ft})\left(\frac{1}{2.65 \times 10^6 \text{ ft-lb/kwh}}\right)\left(\frac{100}{85}\right)$$

$$= 404(E) \text{ kwh/ton Mg}$$

The theoretical energy for the calcination of oyster shell or limestone is approximately 3.9 million Btu/ton of limestone; however, plant operating data are higher at 4.25 million Btu/ton CaO (M-8). Since 3.2 ton of limestone are required per ton of Mg, the calcination energy is

$$(4.25 \times 10^6 \frac{\text{Btu}}{\text{ton lime}})(3.2 \frac{\text{ton lime}}{\text{ton Mg}})(2.94 \times 10^{-4} \frac{\text{kwh}}{\text{Btu}}) = 3998 \text{ kwh/ton Mg}$$

If limestone is utilized, a preliminary grinding step is necessary. Commercial limestone grinders require typically 40 HP for 3/4 ton of feed every hour (M-4) which results in an energy requirement of

$$\left(\frac{3.2 \times 40 \text{ HP}}{0.75 \text{ ton/hr}}\right)(0.74 \text{ kwh/HP hr}) = 126(E) \text{ kwh/ton Mg}$$

Energy for mixing lime and sea water in the thickener and lime preparation from $CaCO_3$ are given below.

For every ton of $Mg(OH)_2$ treated per day, a 100 ft^2 thickener with an energy consumption of 0.05 HP is adequate (M-6). Since 2.4 ton of $Mg(OH)_2$ are needed per ton of Mg, the energy is

$$(2.4 \frac{\text{ton } Mg(OH)_2}{\text{ton Mg}})(0.05 \frac{HP}{\text{ton } Mg(OH)_2/\text{day}})(24 \frac{hr}{day})(0.74 \frac{kwh}{HP\text{-}hr})$$

$$= 2.1(E) \text{ kwh/ton Mg}$$

The energy for the lime slaker can be calculated similarly to give a value of 15(E) kwh/ton Mg.

2. Concentration of $MgCl_2$. The $MgCl_2$ is concentrated from 15 to 74% by weight in direct fired evaporators and 5.32 lb of water must be evaporated per ton of $MgCl_2$. The theoretical energy requirement for this step is,

$$(5.32 \frac{\text{lb steam}}{\text{lb } MgCl_2})(\frac{95 \text{ lb } MgCl_2}{24.3 \text{ lb Mg}})(\frac{2.9 \times 10^{-4} \text{ kwh/Btu}}{0.001036 \frac{\text{lb steam at } 212°F}{\text{Btu}}})(2000 \text{ lb/ton})$$

$$= 11{,}644 \text{ kwh/ton Mg}$$

The average thermal efficiency of these evaporators is close to 25% (M-10), yielding an actual energy requirement of 46,575 kwh/ton Mg. Typical operating data quoted by the Bureau of Mines (M-10) is 150 million ft^3 of gas/ton of Mg. This figure gives an energy consumption of 45,000 kwh assuming a 1000 Btu/ft^3 calorific value (M-5).

3. Electrolysis of $MgCl_2$. The energy for $MgCl_2$ decomposition is divided into two parts: energy for electrolysis and energy associated with anode replacement. Operating cell performances indicate a power requirement of 7 kwh/lb of Mg or 14,000(E) kwh/ton Mg (M-2) for the electrolysis. Per ton of Mg, 0.1 ton of graphite is consumed (M-10). The energy expenditure for fabricating 0.1 ton of electrolytic graphite is ~700 kwh (M-7), 600 kwh of which is electrical energy and the rest is coal.

4. Hydrochloric Acid Recovery. The basic reaction is:

$$CH_4 + 2Cl_2 + O_2 \rightarrow 4HCl + CO_2$$

Now 2 moles of HCl are needed per mole of $MgCl_2$; hence the methane consumption per lb of Mg is 16/48 = 0.3 lb. This corresponds to an energy expenditure of

$$(1000 \frac{\text{Btu}}{ft^3 \text{ gas}})(23.8 \frac{ft^3 \text{ gas}}{\text{lb } CH_4})(0.3 \frac{\text{lb } CH_4}{\text{lb Mg}})(3 \times 10^{-4} \frac{kwh}{\text{Btu}})(2000 \frac{\text{lb}}{\text{ton}})$$

$$= 4284 \text{ kwh/ton Mg}$$

12.1.2 Calculation of the Gibbs Free Energy Change

The reactions occurring at the various stages of the process are summarized below:

$$CaCO_3 \rightarrow CaO + CO_2$$

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$MgCl_2 + Ca(OH)_2 \rightarrow CaCl_2 + Mg(OH)_2$$

$$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$$

$$MgCl_2 \rightarrow Mg + Cl_2$$

$$Cl_2 + \tfrac{1}{2}CH_4 + \tfrac{1}{2}O_2 \rightarrow 2HCl + \tfrac{1}{2}CO_2$$

The overall reaction is represented as,

$$CaCO_3 + MgCl_2 + \tfrac{1}{2}CH_4 + \tfrac{1}{2}O_2 \rightarrow \tfrac{3}{2}CO_2 + Mg + H_2O + CaCl_2$$

Products	$\Delta F°$, kcal/gmole	Reactants	$\Delta F°$, kcal/gmole
$\frac{3}{2}CO_2$	-141	$CaCO_3$	-270.8
Mg	0	$MgCl_2$	-143.8
H_2O	- 54.6	$\frac{1}{2}CH_4$	- 6
$CaCl_2$	-195.4	$\frac{1}{2}O_2$	0
	-391		-420.6

∴ Gibbs Free Energy Change for the overall process

$$= (\Delta F°)_{products} - (\Delta F°)_{reactants}$$

$$= -391 + 420.6 = 29.6 \text{ kcal/gmole of Mg}$$

$$\therefore \quad \Delta F^\circ = \left(29.6 \frac{\text{kcal}}{\text{mole Mg}}\right)\left(\frac{1}{24 \text{ g/mole}}\right)\left(\frac{10^6 \text{ g/long ton}}{1.1 \frac{\text{long ton}}{\text{short ton}}}\right)\left(1.1 \times 10^{-3} \frac{\text{kwh}}{\text{kcal}}\right)$$

$$= 1233 \text{ kwh/ton Mg}$$

12.2 Aluminum

12.2.1 Aluminum Production from Bauxite

The energy requirements for Al production from the Bayer Process using bauxite are outlined below.

The electrical energy consumption in mixing, crushing, grinding, and jigging of the bauxite is estimated to be 200-300(E) kwh/ton of alumina. This figure was obtained from the Aluminum Company of America (A-1) for a typical 50% Al_2O_3 containing rock obtained by open pit mining. Since two tons of alumina produce approximately one ton of refined aluminum after electrolysis (A-9), the pretreatment energy is 500(E) kwh/ton Al. If a poorer grade bauxite (30% Al_2O_3) is used, three tons of ore are needed to obtain a ton of alumina. The corresponding energy requirement is 650(E) kwh/ton of alumina or 1300(E) kwh/ton Al.

A common steam circuit is generally used for both the digestion and evaporation (A-4). Actual plant data indicate 7.875 lb of steam at 300 psig (800 Btu/lb) are consumed per lb of alumina (A-4). An 80% energy efficiency has been assumed for the conversion of coal energy to steam; therefore, for a 50% Al_2O_3 the energy requirement is

$$\left(7.875 \frac{\text{lb steam}}{\text{lb } Al_2O_3}\right)\left(\frac{2 \text{ lb } Al_2O_3}{\text{lb Al}}\right)\left(\frac{2000 \text{ lb}}{\text{ton}}\right)\left(800 \frac{\text{Btu}}{\text{lb steam}}\right)\left(2.93 \times 10^{-4} \frac{\text{kwh}}{\text{Btu}}\right)$$

$$= 7384 \text{ kwh/ton Al}$$

$$\text{equivalent coal energy} = \frac{7384}{0.8} = 9230 \text{ kwh/ton Al}$$

For a 30% Al_2O_3 bauxite, 1.67 times the ore has to be processed per ton of Al. Since the amount of silica increases by this ratio, there is a proportionate increase in the caustic consumption for digestion. Since overall caustic consumption is nominal, no energy expenditure has been included for caustic makeup. As a first approximation the energy for the steam would increase to (5/3)(7384) = 12,306 kwh/ton Al, and the equivalent coal energy is 15,383 kwh/ton Al.

Based on existing plant data, pumping, clarification, and filtration require around 50(E) kwh/ton Al (A-1).

The calcination of the trihydrate to alumina is generally performed in a gas fired rotary kiln. Approximately 1940 Btu/lb of Al_2O_3 have to be supplied (A-2). This corresponds to an energy requirement of

$$(1940 \frac{Btu}{lb\ Al_2O_3})(\frac{2\ lb\ Al_2O_3}{lb\ Al})(2000 \frac{lb}{ton})(2.93 \times 10^{-4} \frac{kwh}{Btu})$$

$$= 2281 \text{ kwh/ton Al}$$

Electrolysis of alumina consumes considerable energy and is conveniently divided into two separate categories:

Energy for electrolysis. As discussed in Sect. 5.1, although current efficiency is 85-90%, the voltage efficiency is low (~40%). The overall power consumption including bus bar losses for a well designed cell is around 7(E) kwh/lb Al or 14,000(E) kwh/ton Al. (A-8).

Energy expenditures associated with the replacement of consumable carbon anodes are small compared to the electrolysis. For every ton of Al produced at the cathode, approximately 0.5 ton of the anode is consumed. The energy involved in preparation of the anode has been estimated at around 7000 kwh/ton (see Sect. 12.1.1) or ~3500 kwh/ton Al.

12.2.2 Calculation of the Gibbs Free Energy Change

The reactions involved in the process are:

$$Al_2O_3 \cdot 3H_2O \rightarrow Al_2O_3 + 3H_2O$$

$$Al_2O_3 \rightarrow 2Al + \frac{3}{2}O_2$$

$$\frac{3}{2}O_2 + \frac{3}{2}C \rightarrow \frac{3}{2}CO_2 \text{ (anode reactions)}$$

The overall reaction is

$$Al_2O_3 \cdot 3H_2O + \frac{3}{2}C \rightarrow 2Al + 3H_2O + \frac{3}{2}CO_2$$

$$(\Delta F^\circ) = (\Delta F^\circ)_{products} - (\Delta F^\circ)_{reactants}$$

Reactants	$\Delta F°$, kcal/gmole	Products	$\Delta F°$, kcal/gmole
$Al_2O_3 \cdot 3H_2O$	-547	2Al	0
$\frac{3}{2}C$	0	$3H_2O$	-168
		$\frac{3}{2}CO_2$	-141.4
Total	-547		-309.4

$$\therefore \quad \Delta F° = -309.4 + 547 = 237.6 \text{ kcal/2 mole of Al}$$

$$= 118.8 \text{ kcal/mole Al}$$

$$= 118.8 \ \frac{\text{kcal}}{\text{mole}}\left(\frac{1 \text{ mole}}{27 \text{ gm}}\right)\left(\frac{10^6 \text{ gm}}{\text{long ton}}\right)\left(\frac{1}{1.1 \ \frac{\text{short ton}}{\text{long ton}}}\right)\left(1.1 \times 10^{-3} \ \frac{\text{kwh}}{\text{kcal}}\right)$$

$$= 4400 \text{ kwh/ton Al}$$

12.2.3 Aluminum Production from Clay

The energy requirements for obtaining alumina from clay have been estimated by the U.S. Bureau of Mines (A-5). To this estimate the energy for the electrolysis (same as Bayer Process) and for the preparation of nitric acid must be added. Fourteen one hundredths ton of nitric acid are consumed per ton of Al. Nitric acid is made from ammonia which in turn is synthesized from natural gas. Five hundred seventy four pounds of NH_3 are needed for a ton of HNO_3 and the energy requirements for a ton of ammonia are 60(E) kwh and 19,200 ft^3 of natural gas at STP. Hence the energy consumption in the manufacture of 574 lb of NH_3 is

$$\frac{574}{2000}\left[.4 + 19{,}200 \text{ ft}^3\left(1000 \ \frac{\text{Btu}}{\text{ft}^3}\right)\left(2.93\times10^{-4} \ \frac{\text{kwh}}{\text{Btu}}\right)\right] = 1658 \text{ kwh/574 lb } NH_3$$

In the production of HNO_3 1750 lb of steam and 9(E) kwh are consumed. Hence the total energy requirement in generating the HNO_3 from natural gas is (A-7)

$$1658 + .4 + 1750 \text{ lb}(900 \text{ Btu/lb})(2.93\times10^{-4} \text{ kwh/Btu}) = 2142 \text{ kwh/ton } HNO_3$$

For one ton of Al this corresponds to 0.14(2142) = 300 kwh/ton Al.

A summary of the energy needs for the entire process is given in Table 5, Sect. 5.2

12.2.4 Aluminum Production from Anorthosite

The U.S. Bureau of Mines has estimated the primary energy requirements. To this estimate one must add the energy associated with soda ash preparation and limestone grinding.

1. Soda Ash Preparation. One half of a ton of bituminous coal is consumed in producing one ton of soda ash, and 0.17 ton of soda ash is used per ton Al. If a calorific value of 14,000 Btu/lb for the coal is assumed, the energy is (A-6)

$$\left(\frac{0.5 \text{ ton coal}}{\text{ton soda ash}}\right)\left(\frac{0.17 \text{ ton soda}}{\text{ton Al}}\right)\left(14{,}000 \frac{\text{Btu}}{\text{lb coal}}\right)\left(2000 \frac{\text{lb}}{\text{ton}}\right)\left(2.93 \times 10^{-4} \frac{\text{kwh}}{\text{Btu}}\right) = 697 \text{ kwh/ton Al}$$

2. Limestone Grinding. An expenditure of 40 HP is needed to grind limestone at a rate of 0.75 ton/hr, and 17.6 tons of limestone are needed per ton of Al (A-3). This gives an energy requirement of

$$\left(\frac{40 \text{ HP}(17.6)}{0.75 \text{ ton/hr}}\right)\left(0.74 \frac{\text{kwh}}{\text{HP-hr}}\right) = 695(E) \text{ kwh/ton Al}$$

12.3 Iron

12.3.1 Iron Production

Energy requirements for the various steps in iron production were obtained from published literature (I-1, 2, 5, 7, 9) and various research articles (I-4, 6, 8). When information on ore beneficiation was not directly available, energy consumption was estimated based on the average practice in the iron industry and design data obtained by Taggardt (I-8).

Sample calculations are based on magnetic taconites. For this and all other ores, the following range of energy consumptions were used when no information was found (I-8).

	Electric Energy, kwh/ton ore
Crushing or grinding	10-27
Spiralling	0.8
Tabling	0.8-1.0
Flotation	1-4

	Electric Energy, kwh/ton ore
Magnetic concentration	1-2
High intensity magnetic concentration	3-5
Tailings disposal	1-1.5
Miscellaneous (pumping, heating, etc.)	1-1.5

12.3.1.1 Mining and Beneficiation of Taconites (32.5% Fe, 43% SiO_2).

(1) Blasting requires 16 tons NH_4NO_3 explosive per 46,000 tons of ore extracted (I-7). The equivalent coal energy involved in the manufacture of this explosive is calculated from Ref. (I-3) as follows:

NH_4NO_3 is manufactured from NH_3 and HNO_3. Per ton of explosive 0.22 ton NH_3, 0.815 ton HNO_3, 2.8 ton of 250 psig steam, and 49.5 kwh of electricity are consumed. The energy consumption per ton of NH_3 and HNO_3 was calculated in Appendix 12.2.3 to be 5777 kwh and 2142 kwh, respectively. Therefore, per ton of NH_4NO_3 the energy consumption is

$$(0.22)(5777) + (0.815)(2142) + (2.8)(2000)(1150)(1.25)(2.93 \times 10^{-4}) + 49.5(2.5) = 5500 \text{ kwh/ton } NH_4NO_3$$

$$\text{and the energy associated in blasting} = \frac{16}{46{,}000}(8915)\left(\frac{1}{0.32 \text{ ton Fe/ton crude}}\right)$$

$$= 6.0 \text{ kwh/ton Fe}$$

The energy requirements for drilling were calculated and found to be negligible ($\sim$0.001 kwh/ton Fe).

(2) The stripping energy which includes the separation and transportation of the overburden was estimated at 1.5 kwh/ton crude or 4.7(E) kwh/ton Fe.

(3) Energy requirements for crushing the ore have been estimated at 3.5 kwh/ton crude. This is equivalent to 11(E) kwh/ton pig iron (I-7).

(4) Grinding of the ore in ball and rod mills is more energy consuming than crushing (I-7).

$$17 \text{ kwh/ton crude}(1 \text{ ton crude}/0.32 \text{ ton Fe}) = 53(E) \text{ kwh/ton Fe}$$

(5) Magnetic concentration (low intensity) of the ore requires 1.5 kwh/ton crude or approximately 5(E) kwh/ton iron (I-7).

(6) Pelletization of the beneficiated ore is performed around 2000°F and involves an oxidation reaction as well as an agglomeration step. The thermal energy requirements for taconites vary from 0.425 to 0.525 million Btu/ton of pellets, while the specular hematites require 1.0 to 1.6 million Btu/ton of pellets (I-7, 5). The taconites require less energy because the oxidation of Fe_3O_4 to Fe_2O_3 is exothermic and supplies a part of the overall heat requirements. Therefore, for taconites:

$$(500{,}000 \frac{\text{Btu}}{\text{ton pellets}})(\frac{\text{ton pellet}}{0.63 \text{ ton Fe}})(2.93 \times 10^{-4} \frac{\text{kwh}}{\text{Btu}}) = 225 \text{ kwh/ton Fe}$$

For other ores:

$$(1.5 \times 10^{6} \frac{\text{Btu}}{\text{ton pellets}})(\frac{\text{ton pellets}}{0.63 \text{ ton Fe}})(2.93 \times 10^{-4} \frac{\text{kwh}}{\text{Btu}}) = 698 \text{ kwh/ton Fe}$$

(7) Miscellaneous energy consumptions include pumping, tailings disposal, and operation of accessory equipment. These energies vary widely depending on the type of operation and plant efficiencies. Typical operating data for one plant (I-7) show approximately 9(E) kwh/ton.

12.3.1.2 Chemical Reduction of the Ore.

(1) Blast Furnace Operation. Energy requirements of a blast furnace vary from 2700 kwh to 3300 kwh/ton of pig iron depending on the ore purity, heat transfer, contacting efficiency, and heat recovery schemes employed. Table 17 gives operating data (material and energy balances) for a typical furnace using beneficiated taconite pellets (63% Fe, 8% SiO_2) (I-1).

(2) Electric Smelting Furnace. This method of iron reduction has not gained popularity because of the very high energy consumptions involved: 2200 kwh of electrical energy and 2738 kwh of coal energy per ton of pig iron. Table 18 gives raw materials and energy consumptions for a typical electric furnace (I-1). The equivalent coal energy is 8238 kwh/ton pig iron which is substantially higher than for a blast furnace.

12.3.1.3 Calculation of Gibbs Free Energy Change. The overall reaction representative of the process is given as,

$$3Fe_2O_3 + 9C + \frac{9}{2}O_2 \rightarrow 6Fe + 9CO_2$$

Table 17. Operating Data for a Typical Blast Furnace (I-1) Using Beneficiated Taconite Pellets (63% Fe, 8% SiO_2)

Basis: 1 ton pig iron (3.8% C, 0.8% Si, 0.8% Mn, 0.02% S, 0.016% P)
Typical Production Rate: 4400 ton/day
Air Blast Temperature: 219°F
Fuel Oil Consumption: 100 lb

1.	Raw Materials	lb	
	Taconite pellets	3040	
	Iron and steel scrap	54	
	Coke	1197	
	Limestone	522	
2.	Energy Balance		
	1. Energy Input	kwh	
	a) Chemical enthalpy change	2646	
	b) Sensible heat in air blast	432	
	c) Slag reactions	41	
	Total	3119	kwh/ton iron
	2. Energy Output	kwh	
	a) Sensible heat - off-gases	173	
	b) Sensible heat - metal	320	
	c) Sensible heat - slag	190	
	d) Calcination of limestone	88	
	e) Reduction of iron oxides	1714	
	f) Other reactions	290	
	g) Heat losses	344	
	Total	3119	kwh/ton iron

Table 18. Material and Energy Balances for the Production of One Ton Pig Iron (3.8% C, 0.8% Si, 0.8% Mn) in an Electric Smelting Furnace (I-1)

Electric Furnace Rating: 33,000 kva
Typical Production Rate: 90 ton/day pig iron
Composition of Feed: 63% Fe, 7.8% SiO_2

1. Raw Materials	
Iron ore pellets	2000 lb
Iron and steel scrap	200 lb
Coke	680 lb
Limestone	299 lb
2. Energy Input	
Calorific value of coke used	2738 kwh
Electrical Energy	2200(E) kwh
	2200(E) + 2738 kwh/ton iron

Equivalent coal energy = 8238 kwh/ton iron

Reactants	$\Delta F°$, kcal/gmole	Products	$\Delta F°$, kcal/gmole
$3Fe_2O_3$	- 179.1	$9CO_2$	- 94.26
9C	0	6Fe	0
$\frac{9}{2}O_2$	0		

$$\therefore \quad \Delta F°_{overall} = 9(-94.26) - 3(-179.1)$$

$$= -311 \text{ kcal/6 gmoles Fe}$$

$$= \left(\frac{-311}{(6)(58)}\right)(454)\left(2000 \frac{\text{kcal}}{\text{ton Fe}}\right)\left(1.16 \times 10^{-3} \frac{\text{kwh}}{\text{kcal}}\right)$$

$$= -941.3 \text{ kwh/ton}$$

12.3.3 Ore Beneficiation Flowsheets

Figures 11, 12, and 13 are proposed flowsheets for beneficiation plants based on non-magnetic taconite, specular hematite, and iron laterite ores, respectively. Each of these processes have been described briefly in Sect. 6.2.

12.4 Copper

12.4.1 Energy for Copper Production

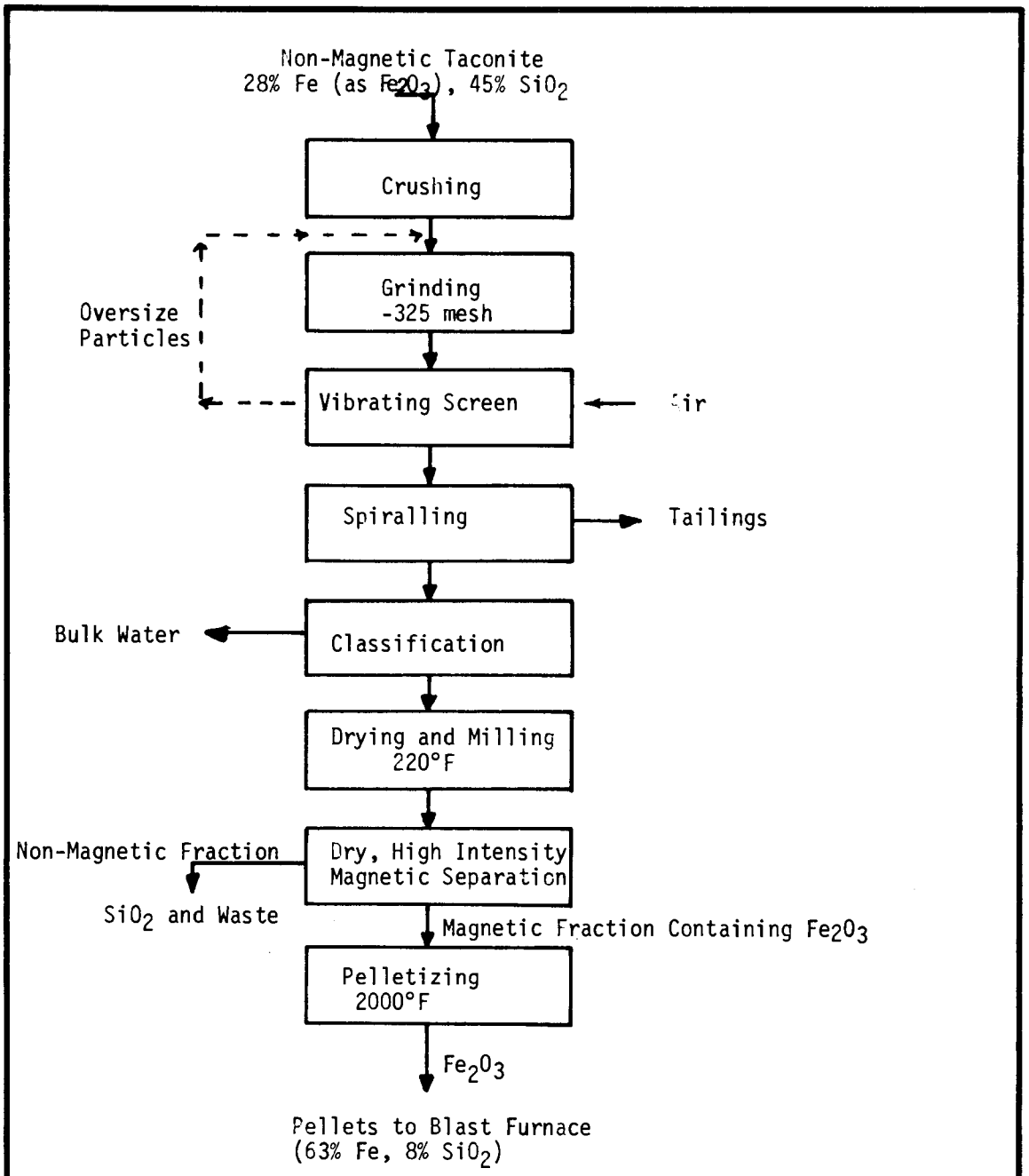
The energy requirements associated with the production of copper metal from virgin ores is divided into beneficiation, smelting and refining.

1. Beneficiation. The energy requirements for mining is dependent on the blasting [for one open pit mine 0.00015 t NH_4NO_3/t crude ore (C-7). With modern mining techniques approximately 20 hp-hr of energy are required per ton of crude ore (C-1). For a 1% copper ore and with a 90% recovery in the beneficiation step, the energy requirement is calculated to be:

$$\left[\frac{0.00015 \text{ t } NH_4NO_3}{\text{t crude}}\left(\frac{9430 \text{ kwh}}{\text{t } NH_4NO_3}\right) + (2.5)\left(\frac{20 \text{ hp-hr}}{\text{t crude}}\right)\left(0.745 \frac{\text{kwh}}{\text{hp-hr}}\right)\right.$$

$$\left. \times \left(\frac{100 \text{ t crude}}{0.9 \text{ t Cu}}\right)\right] = 4296 \text{ kwh/ton Cu}$$

Of the energy consumed in beneficiation, crushing consumes 19%, grinding 53%, ore flotation 12%, and the rest for miscellaneous uses.



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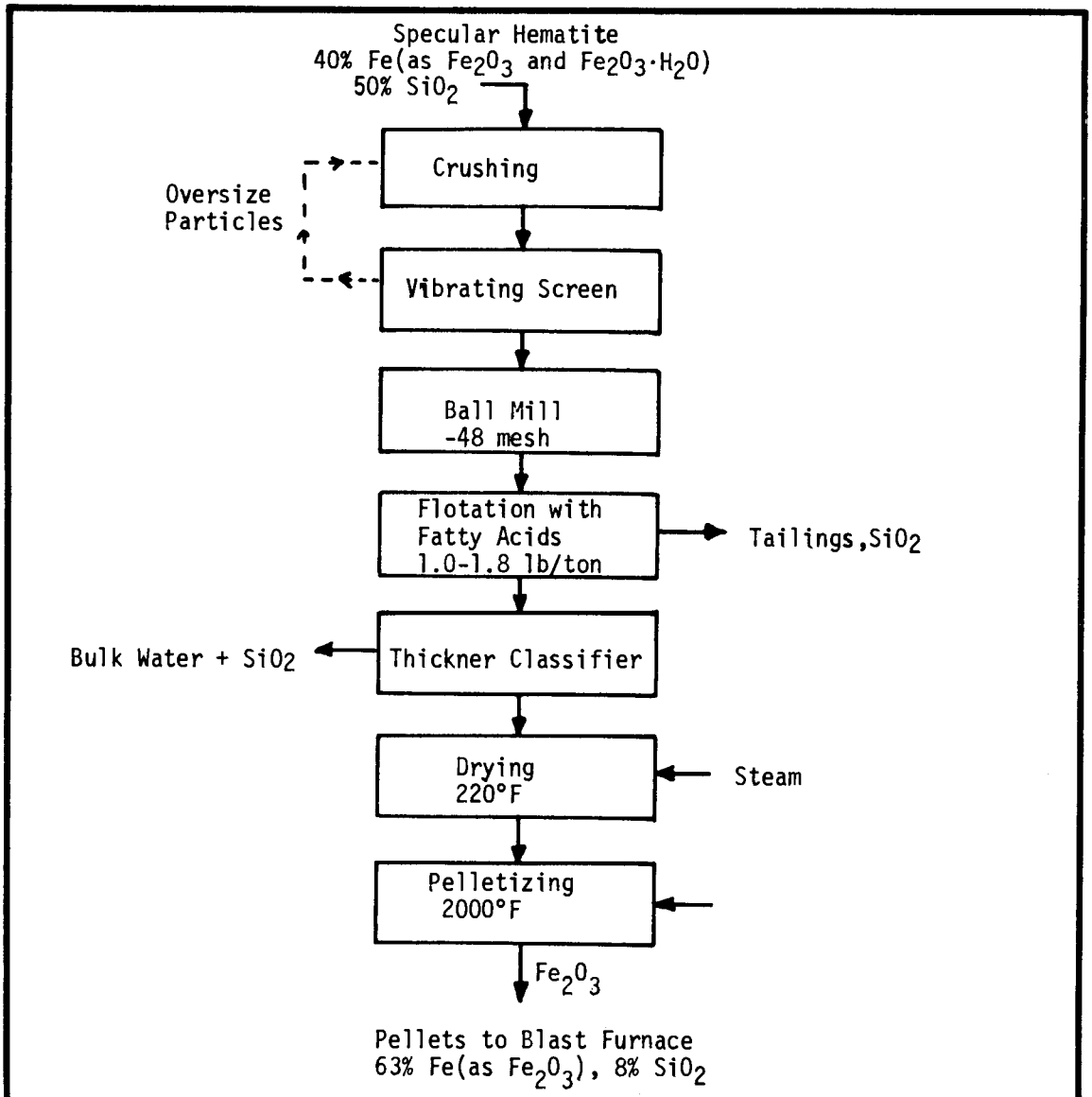
Proposed Flowsheet Beneficiation
of Non-Magnetic Taconite (I-1,2)

DATE	DRAWN BY	FILE NO.	FIG.
5-25-71	CF	CEPS-X-132	11



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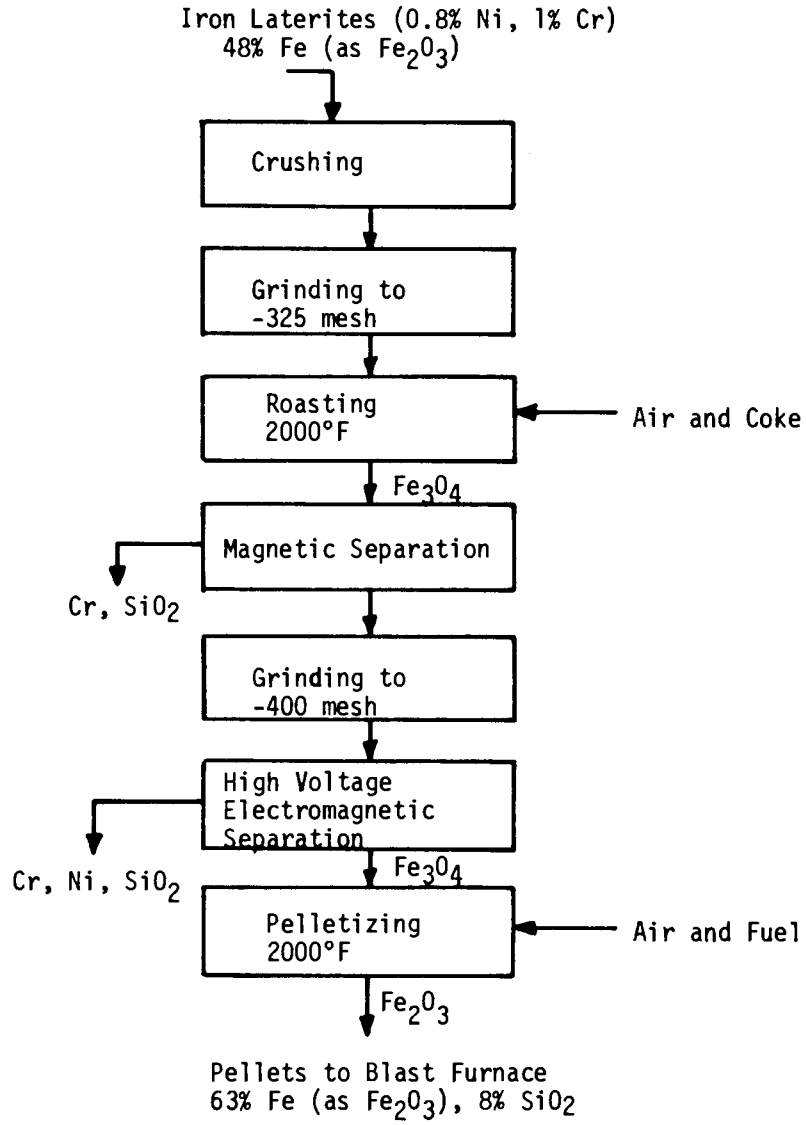
Proposed Flowsheet for Beneficiation of Specular Hematite Ores (I-1)

DATE	DRAWN BY	FILE NO.	FIG.
5-25-71	JCB	CEPS-X-132	12



NOTE: Pelletizing is also an oxidation step.

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Proposed Flowsheet for Beneficiation of Iron Laterites (I-4)

DATE	DRAWN BY	FILE NO.	FIG.
5-25-71	JCB	CEPS-X-132	13

Lime (6 lb/ton of ore) is generally used in the flotation process along with small amounts of other chemicals. Since 1465 kwh of energy is necessary for lime calcination (1 ton) (C-6), this corresponds to an energy equivalent of

$$(6)(\frac{1}{0.01})(\frac{1}{0.9})(\frac{1}{2000})(1465) = 488 \text{ kwh/ton Cu}$$

In addition to the calcination the limestone has to be crushed before sending it to the furnace. Forty hp-hr are needed to crush 3/4 ton of limestone (see Appendix 12.1.1). Hence the energy requirement is

$$(\frac{40}{0.75})(\frac{6}{(0.01)(0.9)})(\frac{1}{2000 \text{ lb/ton}})(0.745 \frac{\text{kwh}}{\text{hp-hr}}) = 13.25(E) \text{ kwh/ton Cu}$$

2. Smelting. Some copper smelters roast the concentrate before it is introduced to the reverberatory furnace to reduce the sulfur content of the concentrate for optimum treatment. The reverberatory furnaces are generally fueled by natural gas, fuel oil, or pulverized coal. Irrespective of fuel it requires about 3×10^6 Btu to melt one ton of solid charge when charged hot, to 6×10^6 Btu when the solid charge is cold and contains up to 10% H_2O (C-7, 3). For a 25% copper concentrate this corresponds to 7032 kwh/ton Cu.

Pulverization of bituminous coal requires approximately 15 kwh(E)/ton (C-5). If 12,000 Btu/lb of coal is assumed, the pulverization of coal requires 15 kwh/ton Cu.

The amount of silica and limestone added as fluxes to the reverberatory charge varies with concentrate concentrations (C-13). If it is assumed that silica and limestone consumptions are 0.8 and 0.25 ton/ton Cu, respectively, the energy requirements can be calculated. Eighty hp-hr of energy are needed to crush 1.25 ton of silica (C-12). Hence the energy requirements are:

$$(\frac{80 \text{ hp-hr}}{1.25 \text{ ton silica}})(\frac{0.8 \text{ ton silica}}{\text{ton Cu}})(0.745 \frac{\text{kwh}}{\text{hp-hr}}) = 38(E) \text{ kwh/ton Cu}$$

Similarly energy for crushing the limestone is 10(E) kwh/ton Cu.

3. Refining. The energy requirement for the refining furnace is about 3.5×10^6 Btu of gas/ton Cu produced or 1025 Btu/ton of Cu (C-5). Electrorefining of copper using a well designed electrolytic cell requires 200 kwh/ton of refined product (C-8). The additional heating and chemical requirements are negligible.

12.4.2 Gibbs Free Energy Change

The Gibbs Free Energy Change for the production of Cu from sulfide ore is calculated assuming a zero free energy of mixing of the Cu_2S in the ore.

The overall reaction is

$$Cu_2S + O_2 \rightarrow 2Cu + SO_2$$

Reactants	$\Delta F°$ kcal/gmole	Products	$\Delta F°$ kcal/gmole
Cu_2S	-158.3	Cu	0
O_2	0	SO_2	- 71.68

$$(\Delta F°)_{overall} = (\Delta F°)_{products} - (\Delta F°)_{reactants}$$

$$= -71.68 - (-158.3) \approx 86.6 \text{ kcal/2 moles Cu}$$

$$\Delta F° = \left(\frac{86.6 \text{ kcal}}{2 \text{ gmole Cu}}\right)\left(\frac{1 \text{ gmole Cu}}{63.5 \text{ g Cu}}\right)\left(\frac{454 \text{ g}}{1 \text{ lb}}\right)\left(\frac{2000 \text{ lb}}{1 \text{ ton}}\right)\left(\frac{0.00116}{1} \frac{\text{kwh}}{\text{kcal}}\right)$$

$$= 718.22 \text{ kwh/ton Cu}$$

12.4.3 Recovery of Co-Products and By-Products

For every ton of anode mud obtained from the electrorefining of impure copper, the following by-products can be recovered (C-11): gold (9.38 lb), silver (412.5 lb), selenium (150 lb), and tellurium (30 lb). The energy requirements in each step of the process are outlined below (basis: one ton anode mud).

1. The anode mud contains 15-20% copper which must be leached out with sulfuric acid prior to the recovery of the several by-products. For one ton of mud, 0.81 ton of H_2SO_4 are needed. Energy requirements for H_2SO_4 production at a copper plant are around 150 kwh/ton.

$$0.81 \times 150 = 121(E) \text{ kwh/ton mud}$$

2. Smelting of the leached anode mud is a very energy intensive step. For each ton of anode mud, 110 gal of Bunker "C" fuel oil having a calorific value of 140,000 Btu/gal are used. Hence the energy requirement for the smelting step is,

$$140{,}000 \frac{\text{Btu}}{\text{gal}}\left(110 \frac{\text{gal}}{\text{ton mud}}\right)\left(2.93 \times 10^{-4} \frac{\text{kwh}}{\text{Btu}}\right) = 4512 \text{ kwh/ton mud}$$

3. The electrolysis for the purification of silver and gold requires 0.41(E) kwh/lb of silver, or 169(E) kwh/ton anode mud.

4. SO_2 consumption in the selective precipitation of selenium from tellurium is 2 ton/ton selenium and soda ash consumption is negligible. Since SO_2 is readily available from the converters at a copper plant, no additional energy requirement is considered.

Total energy requirements for gold and silver based on one ton anode mud are 121 + 4512 + 169 = 4802 kwh. Hence on a per ton gold basis the energy is

$$(4802)(\frac{1}{9.38})(2000) = 1.024 \times 10^6 \text{ kwh/ton Au}$$

or

$$\text{per ton of silver} = 4802(\frac{2000}{412.5}) = 2.328 \times 10^4 \text{ kwh/ton Ag}$$

The equivalent coal energies for gold and silver production are 1.117×10^6 kwh and 2.539×10^4 kwh, respectively.

For the selenium and tellurium production in addition to the smelting energy, 50(E) and 75(E), respectively, must be added for the final separation and purification (C-11). Per ton of selenium the equivalent coal energy is 6.59×10^4 kwh and 3.33×10^5 kwh/ton of tellurium.

Since 0.00725 ton anode mud are produced per ton of Cu, the equivalent coal energy per ton Cu to produce the various elements separately has also been calculated. Equivalent coal energy to process one ton mud into gold and silver is

$$(121 + 169)(2.5) + 4512 = 5237 \text{ kwh}$$

$$(5237 \text{ kwh/ton mud})(0.00725 \text{ ton mud/ton copper}) = 38 \text{ kwh/ton copper}$$

Similarly for the selenium and tellurium the additional energy expenditure assuming each element were recovered separately is 35.82 and 36.26 kwh/ton copper, respectively.

12.4.4 Copper Recovery from Scrap Recycle

Two types of copper scrap metals have been studied: 98% Cu scrap metal and impure scrap metal.

1. 98% Cu Scrap. The energy requirements are the latent heat of fusion for the copper plus the thermal energy needed to heat the metal to the melting point (1356°K).

$$\text{energy requirements} = \int_{293}^{1356} (5.49 - 0.0014\,T)dt + 3110 \text{ cal/mole}$$

$$= 5.49(1356 - 293) - \frac{0.0014(1356^2 - 293^2)}{2} + 3110$$

$$= 7.72 \times 10^3 \text{ cal/mole}$$

$$= \frac{7.72 \times 10^6}{65.3} \frac{\text{kcal}}{\text{long ton}} (1.1 \times 10^{-3} \frac{\text{kwh}}{\text{kcal}}) \times (\frac{1}{1.1 \text{ short ton/long ton}})$$

$$= 118(E) \text{ kwh/ton Cu}$$

If a 50% heat transfer efficiency is assumed, the gross energy consumption is 236(E) kwh/ton Cu or an equivalent coal energy of 590 kwh/ton Cu.

2. Recycle of Copper from Impure Scrap Metal. There are many types of impure scrap, and the use of these materials depends largely on the handling and sorting of the scrap. The scrap is primarily used to produce copper alloys where the composition is adjusted by diluting the molten scrap with virgin metals or high-grade scrap.

Some of the impure scrap is refined in the same manner as primary blister copper before it is cast into anodes for electrolytic refining. In addition to the 1025 kwh/ton Cu approximately 5 lb of coke per ton of copper are needed (18.6 kwh/ton Cu).

If a typical scrap metal contains 3% lead and 0.5% arsenic, 30 lb of limestone and 5 lb of soda ash are needed as fluxing agents. The equivalent coal energy for the preparation (chiefly crushing and grinding) of these fluxes is 5 kwh and 10 kwh for the soda ash and limestone, respectively. The energy consumption in the electrorefining step is 200 kwh/ton Cu. Table 11 shows a total energy of 1059 kwh/ton and an equivalent coal energy of 1559 kwh/ton Cu for the recycle from scrap metal.

12.5 Titanium

12.5.1 Titanium Production from Beach Sands

The energy consumption associated with the production of titanium metal from beach sands (1.3% TiO_2, 0.5% Zr) is shown below. The overall process is subdivided into two sections: beneficiation and chemical processing (Kroll Process).

1. Beneficiation.

(a) The energy requirement for blasting is 0.000347 tons NH_4NO_3 explosive per ton of material blasted (T-3).

$$(0.000347 \frac{\text{ton}}{\text{ton ore}})(\frac{1}{0.014 \frac{\text{ton } TiO_2}{\text{ton ore}}})(\frac{79.9 \text{ } TiO_2}{47.9 \text{ Ti}})(9430 \frac{\text{kwh(E)}}{\text{ton}})$$

$$= 391 \text{ kwh/ton Ti}$$

Stripping, hauling, and dredging of the sand require 19 kwh/ton Ti; therefore,

total energy for preliminary extraction = 410(E) kwh/ton Ti

(b) Crushing and grinding of the sand in hammer mills generally consume 1 kwh/ton ore (T-12) which is equivalent to

$$(1)(\frac{1}{0.014})(\frac{79.9}{47.9}) = 120(E) \text{ kwh/ton Ti}$$

(c) Gravity concentration is accomplished by using spiral contactors and rake classifiers. Energy requirements for both are around 0.8 kwh/ton ore (T-12). This corresponds to a total of 190 kwh/ton Ti. Energy requirements for drying are negligible for this process ($\sim$0.01 kwh/ton Ti).

(d) Low intensity magnetic separators consume 1.2 kwh of energy per ton of ore (T-12). This corresponds to an energy requirement of 143(E) kwh/ton Ti.

(e) High voltage electrostatic separators operate at 40,000 v and 15 milliamp current consuming 5.0(E) kwh/ton ore or 550(E) kwh/ton Ti.

(f) Roasting is only necessary when the high alumina clays from the bauxite process are utilized. The roasting converts the iron to a magnetic form for separation from the ilmenite slag. Energy requirements per ton Ti are approximately 2100 kwh/ton Ti.

(g) Miscellaneous energy requirements include (T-3):

disposal of tailings: $(\frac{1.5 \text{ kwh}}{\text{ton ore}})(\frac{1}{0.014})(\frac{79.7}{47.9}) = 180(E)$ kwh/ton Ti

vibrating screens for the jigging operation: $(0.5 \frac{kwh}{ton})(\frac{1}{0.014})$

$$\times (\frac{79.7}{47.9}) = 70(E) \text{ kwh/ton Ti}$$

pumping energy: $(1.2 \frac{kwh}{ton\ ore})(\frac{1}{0.014})(\frac{79.7}{47.9}) = 14.0(E)$ kwh/ton Ti

energy for operating miscellaneous equipment: $\sim$60(E) kwh/ton Ti

(h) The U.S. Bureau of Mines (T-4) has estimated an energy requirement of $\sim$4900(E) kwh/ton of Ti produced in an electric smelting furnace. The iron is removed from the ilmenite concentrate by reduction of the consumable graphite electrode [0.042 ton/ton Ti or $\sim$300 kwh(E)] to produce pig iron and an ilmenite slag ($\sim$86% TiO_2).

2. Chemical Processing (Kroll Process)

(a) Chlorination of the titanium to titanium tetrachloride is an exothermic reaction. However, approximately 0.128 kwh energy/lb $TiCl_4$ is needed to start the process and fluidize the solid phase (T-11); therefore,

$$(0.13 \frac{kwh}{lb\ TiCl_4})(\frac{188\ lb\ TiCl_4}{47.9\ lb\ Ti})(2000 \frac{lb}{ton}) = 1000(E) \text{ kwh/ton Ti}$$

(b) The energy needed for purification of the $TiCl_4$ has been obtained from cost figures provided by the U.S. Bureau of Mines (T-1) to be 2200(E) kwh/ton Ti.

(c) Fuel energy for the magnesium reduction reactor corresponds to 353 gal propane/ton Ti (T-1).

$$(353 \frac{gal}{ton})(90{,}000 \frac{Btu}{gal})(2.93 \times 10^{-4} \frac{kwh}{Btu}) = 9200 \text{ kwh/ton Ti}$$

(d) To maintain the dry room under controlled temperature and humidity conditions, 11,500 kwh energy/ton Ti is expended (T-12).

(e) Ti sponge purification by vacuum distillation requires 6500(E) kwh/ton Ti (T-1).

(f) The electrolytic decomposition of $MgCl_2$ to magnesium and chlorine gas is the most energy intensive step in the whole process. A typical figure for industrial cells is 8.25 kwh/lb Mg (T-6, 13, 14).

$$(8.25 \frac{kwh}{lb\ Mg})(\frac{1\ ton\ Mg}{1\ ton\ Ti})(2000 \frac{lb}{ton}) = 16{,}500(E) \text{ kwh/ton Ti}$$

(g) Energy equivalent corresponding to the consumption of Cl_2, Mg, and carbon in the process is:

Cl_2: (1.5 ton/ton Ti)(3500 kwh/ton Cl_2) = 5200(E) kwh/ton Ti

Mg: (0.1 ton/ton Ti)(90,900 kwh/ton Mg) = 9090 kwh/ton Ti

C: (1.0 ton/ton Ti)(10,000 kwh/ton C) = 10,000 kwh/ton Ti

(h) Energy requirements in a consumable electrode furnace have been estimated at 5500(E) kwh/ton Ti (T-6, 13).

(i) Miscellaneous plant operations are approximately 3000 kwh/ton Ti. (T-14).

12.5.2 Zirconium Co-Product Recovery

Zirconium is recovered as zirconia in the process of beneficiating ilmenite containing ores. The additional energy consumption in the processing of Zr is given below:

(a) Spiral concentrations require 0.7 kwh/ton ore or 140 kwh/ton Zr. This is also equivalent to 95(E) kwh/ton Ti.

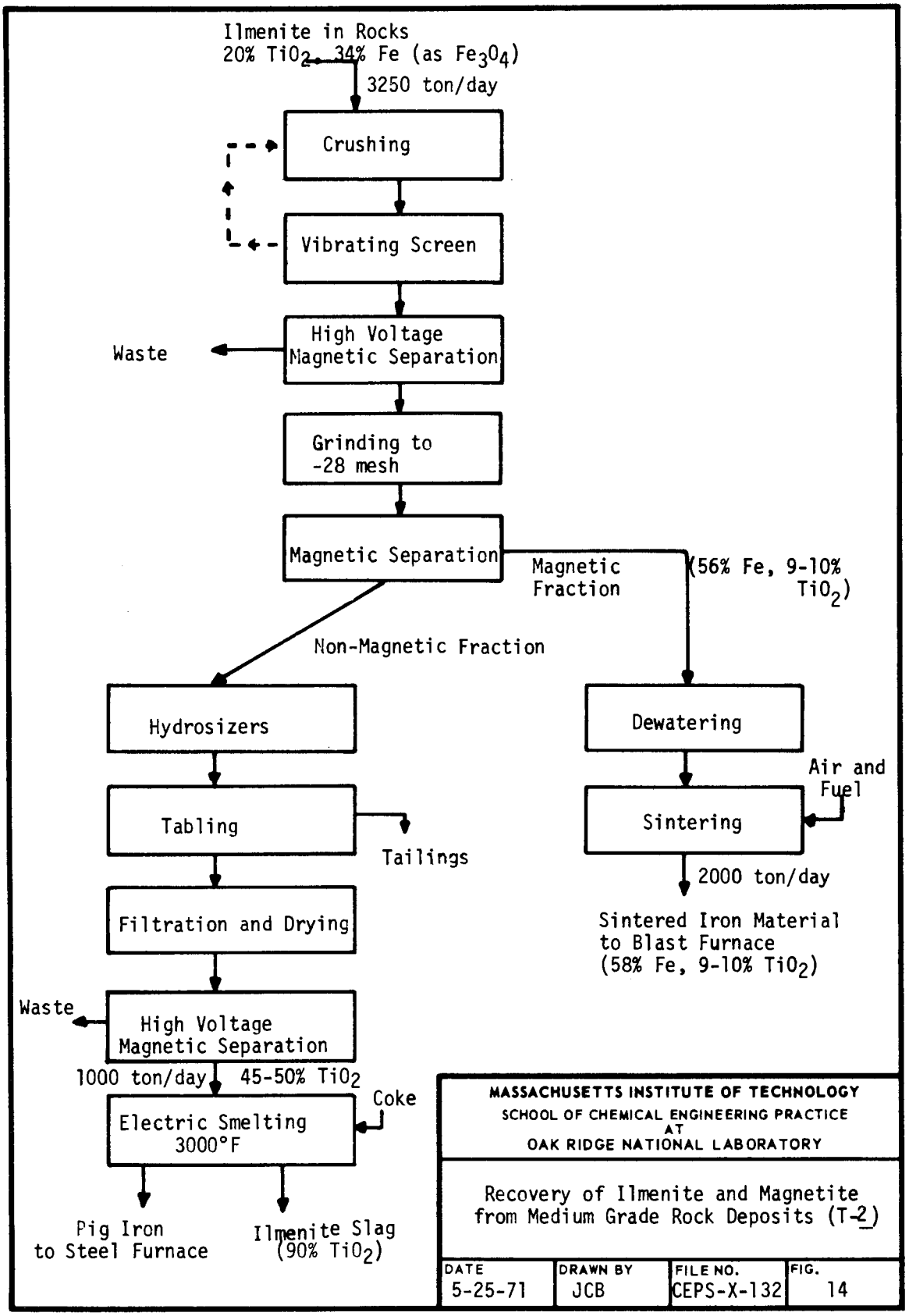
(b) High voltage electrostatic separation involves 5 kwh/ton ore or 550 kwh/ton titanium.

(c) The drying operation at 1200°F has been estimated to consume 20 kwh/ton titanium recovered. Hence the total additional energy for recovering zirconium as zirconia is 650 kwh/ton Ti or 870 kwh/ton Zr. These figures are for a low zirconium content ore and richer ores can result in substantially lower energy requirements.

12.5.3 Beneficiation of Other Titanium Ores

In Sect. 8.1 the process of obtaining ilmenite slag (~90% TiO_2) from beach sands was described. Some of the other lesser important sources of Ti are rock deposits, ferruginous rocks, high titanium clays, and certain types of common soils. A brief description of the beneficiation process for these ores is given below.

(a) Rock deposits (10-20% TiO_2, 34% Fe as Fe_3O_4). Open pit mining of medium grade rock deposits (10-20% TiO_2) requires blasting, hauling, and preliminary crushing of the ore (T-2). The overburden is approximately 2.5 to 3.0 ton/ton finished ore. A typical beneficiating plant is shown in Fig. 14. The more important steps are: (1) Crushing and grinding to minus 28 mesh with intermittent screening and magnetic separation; (2) magnetic separation to remove magnetite and concentrate the non-magnetic ilmenite fraction; (3) hydrosizing, gravity concentration or tabling (20 to 150 mesh) followed by high intensity electromagnetic separation of


Ilmenite in Rocks
20% TiO_2, 34% Fe (as Fe_3O_4)
3250 ton/day
Crushing
Vibrating Screen
High Voltage Magnetic Separation
Waste
Grinding to -28 mesh
Magnetic Separation
Magnetic Fraction
(56% Fe, 9-10% TiO_2)
Non-Magnetic Fraction
Hydrosizers
Tabling
Tailings
Filtration and Drying
Waste
High Voltage Magnetic Separation
1000 ton/day
45-50% TiO_2
Coke
Electric Smelting 3000°F
Pig Iron to Steel Furnace
Ilmenite Slag (90% TiO_2)
Dewatering
Air and Fuel
Sintering
2000 ton/day
Sintered Iron Material to Blast Furnace (58% Fe, 9-10% TiO_2)
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY
Recovery of Ilmenite and Magnetite from Medium Grade Rock Deposits (T-2)
DATE 5-25-71
DRAWN BY JCB
FILE NO. CEPS-X-132
FIG. 14

ilmenite concentrate (45-50% TiO_2); (4) drying and sintering of the magnetite fraction (58% Fe, 9-10% TiO_2) for use in iron blast furnaces.

(b) Ferruginous ilmenite rock deposits (10-35% TiO_2). These cannot be easily concentrated by mechanical means because the Fe_3O_4 in the rock is intimately associated with the titanium mineral (T-7). Upgrading such ores necessitates higher smelting temperatures (above 3000°F) and addition of small quantities of flux, such as lime, in addition to coke. In other cases refining slag in a secondary smelting furnace may be required. Ninety percent TiO_2 slags are obtained, but at the expense of higher energy requirements. A flowsheet for the process is shown in Fig. 15.

(c) High titanium clays. Large tonnages of ilmenite are contained in black sands discarded by plants that treat bauxite by the Bayer Process. In some aluminum plants the sand averages 5% TiO_2. Ilmenite concentrates of 40-41% TiO_2 have been successfully recovered from alumina clays by the Bureau of Mines (T-9). Beneficiation involves crushing and grinding, gravity concentration or tabling, roasting at 1500°F, magnetic and electrostatic separation.

(d) Common soil. Titaniferous soils average 0.2-1.5% TiO_2. These deposits are difficult to beneficiate because of their high gangue content. Important beneficiation steps are: crushing or grinding, gravity concentration, flotation using small amounts of reagents and fatty acids (0.01-0.2 lb/lb ore treated) (T-9), roasting at 1500°F, and magnetic and electrostatic separation.

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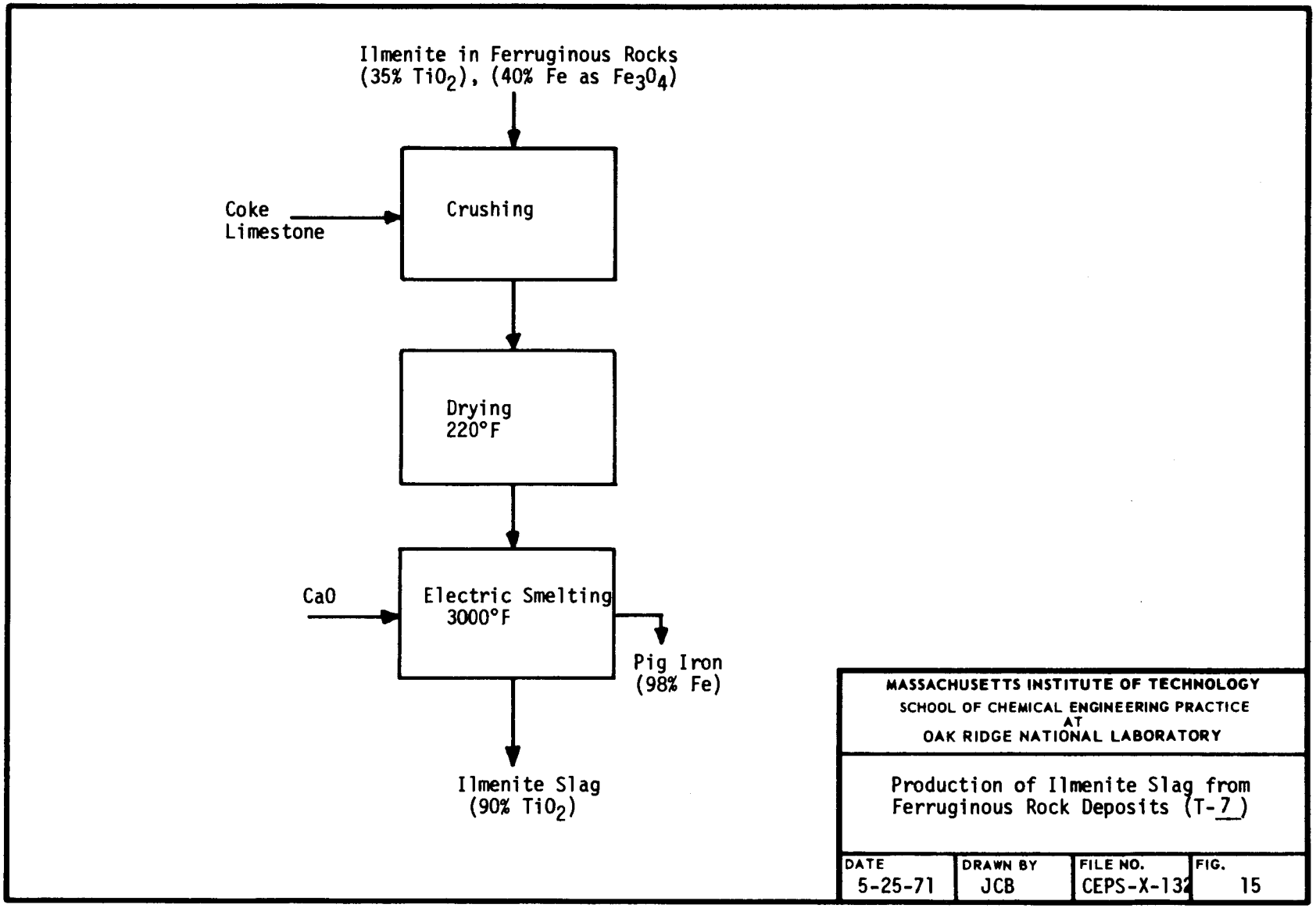
Ilmenite in Ferruginous Rocks
(35% TiO_2), (40% Fe as Fe_3O_4)
Coke
Limestone
Crushing
Drying
220°F
CaO
Electric Smelting
3000°F
Pig Iron
(98% Fe)
Ilmenite Slag
(90% TiO_2)
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL ENGINEERING PRACTICE
AT
OAK RIDGE NATIONAL LABORATORY
Production of Ilmenite Slag from
Ferruginous Rock Deposits (T-7)
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FILE NO.
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FIG.
15

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