

Chapter 5: MATERIAL FLOW IN INDUSTRY

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In this chapter, the learning objectives (LO) will be to:

- Explore the concept of material flow in industry.
- Learn about how material flow contributes to pollution.
- Be introduced to a sustainable economy and the ability to control pollution by controlling material flow.
- Study material flow in the production of steel, aluminum, copper, cement, plastics, paper, and copper oxide. This discussion for steel includes mass balance calculations for the unit operations of mining, pelletizing, pig iron production, and steel production.
- Examine pollution, by-products of primary metal production, and the importance of scrap recycling.

5.5.1 Material Flow Diagrams

Life in our world would be impossible without a large flow of materials, a flow which requires a significant amount of energy and time. For example, in the United States approximately 2-3 tons of ore are mined per person per year, while 6-7 tons of energy-producing materials (coal, oil) are required per person per year. In this materials-oriented society, most people take these materials and the products they produce for granted, with little thought for the necessary “flow of materials” required to get products for use. A generic material flow diagram is illustrated in Fig. 5-1; it depicts the life cycle of a material from its natural state through creation of products to the natural end of its life. This figure is similar to the generic diagram of Ayres,^{*} but includes a time component. The first component, that of location and evaluation of raw materials, is somewhat variable, but will often take 10-20 years or longer, depending upon the material and its location on Earth. In most instances, the time between removal from the earth to production of a product is quite short, much less than either the lifetime of the product or the location and evaluation of raw materials. Obviously, the consumer enters the life cycle at the point of product purchase, with little knowledge or concern about the flow components prior to purchase. In addition, the last step, disposal to a landfill, is usually of no concern for the consumer (with the exception of large products such as automobiles or refrigerators). On this diagram, Fig. 5-1, the materials in the product cease their useful lives. Since matter can neither be created nor destroyed, this last step amounts to a waste of precious resources.

^{*} Robert U. Ayres, “Industrial Metabolism,” in *Technology and Environment*, ed. J. H. Ausubel and H. E. Slackovich (Washington, D.C.: National Academy Press, 1989), pp. 23-49.

Figure 5-1
Material flow Diagram: Disposal in Landfill

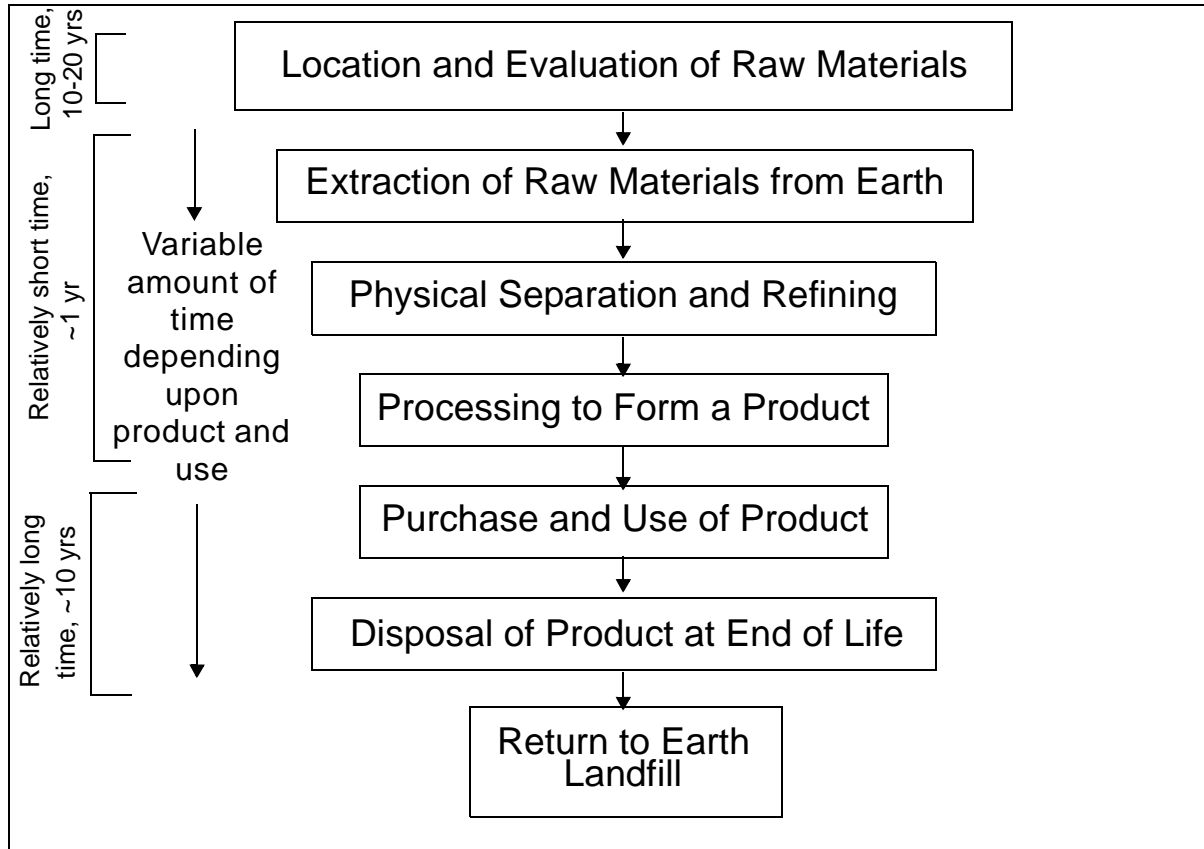
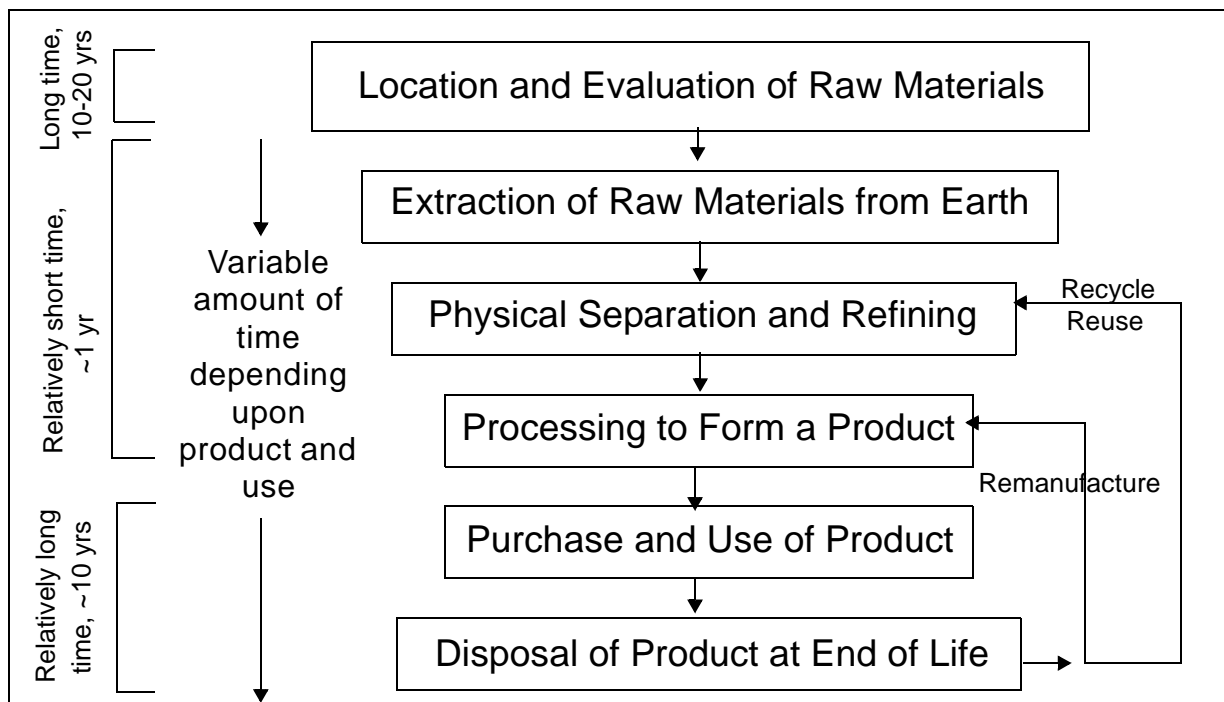


Figure 5-2
Material Flow Diagram: Recycle, Reuse, or Remanufacturing



5.5.2 Closing the Product Life Cycle

The best solution from a resources point of view is to reuse, recycle or remanufacture products so that the life cycle is closed. See Fig. 5-2, where return loops are included into the flow diagram of Fig. 5-1 in place of a step to the landfill. The ideal scenario would involve *every atom* being returned and recycled forever. However, this is not realistic in view of thermodynamic realities of the Second Law, which says that there will be an increase in entropy, a tendency toward randomness in every process. This is seen in the form of wear or corrosion of parts, loss of material to the air or earth during processing, a generation of randomness which cannot easily be reversed. It would be possible to reverse some of these processes, but the energy cost would be so great as to eliminate it from contention. Consider, for example, the cost of recovering iron atoms worn from the surfaces of disc brake rotors or brake drums and deposited on or near the nation's highways, or the cost of recovering the rust particles from automobiles on the same roadways, or the cost of recovering the lead which was used as an additive in gasoline for so many years.

5.5.3 Material Flow and Pollution

The definition of "pollute," as introduced in Chapters 1 and 2, is given below:

Pollute: To introduce a substance or change a medium (air, water, soil, food, etc.) in a way that adversely affects the medium's usefulness.

Each component of the material flow diagrams (Figs. 5-1 and 5-2) provides opportunities for pollution to occur. The loss of lead to the atmosphere and then to the soil during combustion of gasoline is an excellent example of pollution. Lead was originally added to gasoline for the purpose of lubricating valves and providing corrosion protection. Unfortunately, it was determined conclusively that lead (present in the air, water, and soil) is a hazard to health. Since the largest, most easily affected contributor to this pollution came from lead additives to gasoline, federal law required that the lead be removed. Figure 5-3 shows clearly the dramatic impact that reductions in lead in gasoline had on air quality in the U.S.

This is an example of pollution which can be controlled quite easily and effectively.

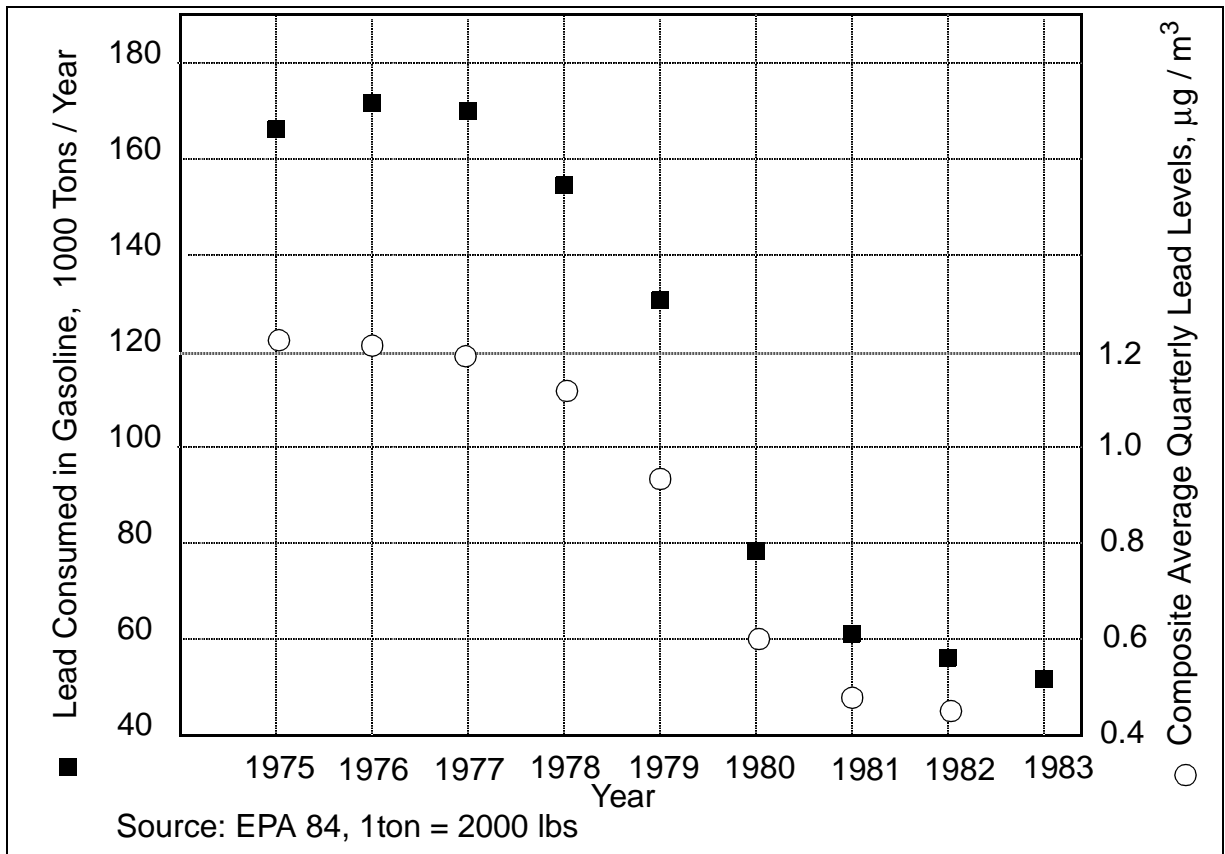


Figure 7 - 3, U.S. Lead Consumed in Gasoline and Ambient Lead Concentrations, 1975 - 1983

It is important to point out that there are some forms of pollution which are understood but are much more difficult to control, pollution which depends upon massive flows of materials in our society. Consider, for example, the concentration of the greenhouse gas CO_2 in the atmosphere as a function of time, Fig. 5-4. The amount of the increase is directly proportional to the amount of carbon-containing fuels that have been mined and burned for energy. Most of the world's significant carbon sources (oil, coal, natural gas) have been located, and there is much concern about the rate at which they are being consumed, both from a pollution point of view (Fig. 5-4) and from the need to create energy. In comparison to other material products, the life cycle of fuel is quite short, less than a year from removal from the earth to combustion. In an ideal situation, the CO_2 generated from combustion returns to the earth through ingestion by plant life. Then the carbon could be recycled again as fuel. Of course, the difficulty with this is that the earth is not capable of converting CO_2 to a combustible form at the rate it is being generated; otherwise, the CO_2 content in the atmosphere would remain constant in Fig. 5-4. The solution to the dilemma created by increased CO_2 (change in world climate with unknown results) is to retreat from fossil fuel combustion and rely more on non-fossil fuel contributions such as nuclear, solar, wind, water, and

hydrothermal. While this change is inevitable, it will happen only gradually as the efficiencies of the alternative energy sources increase. Unlike the quick action observed in lead contamination in the U.S., reduction in atmospheric CO₂ will come only after further increases, a very slow and uncertain process at best.

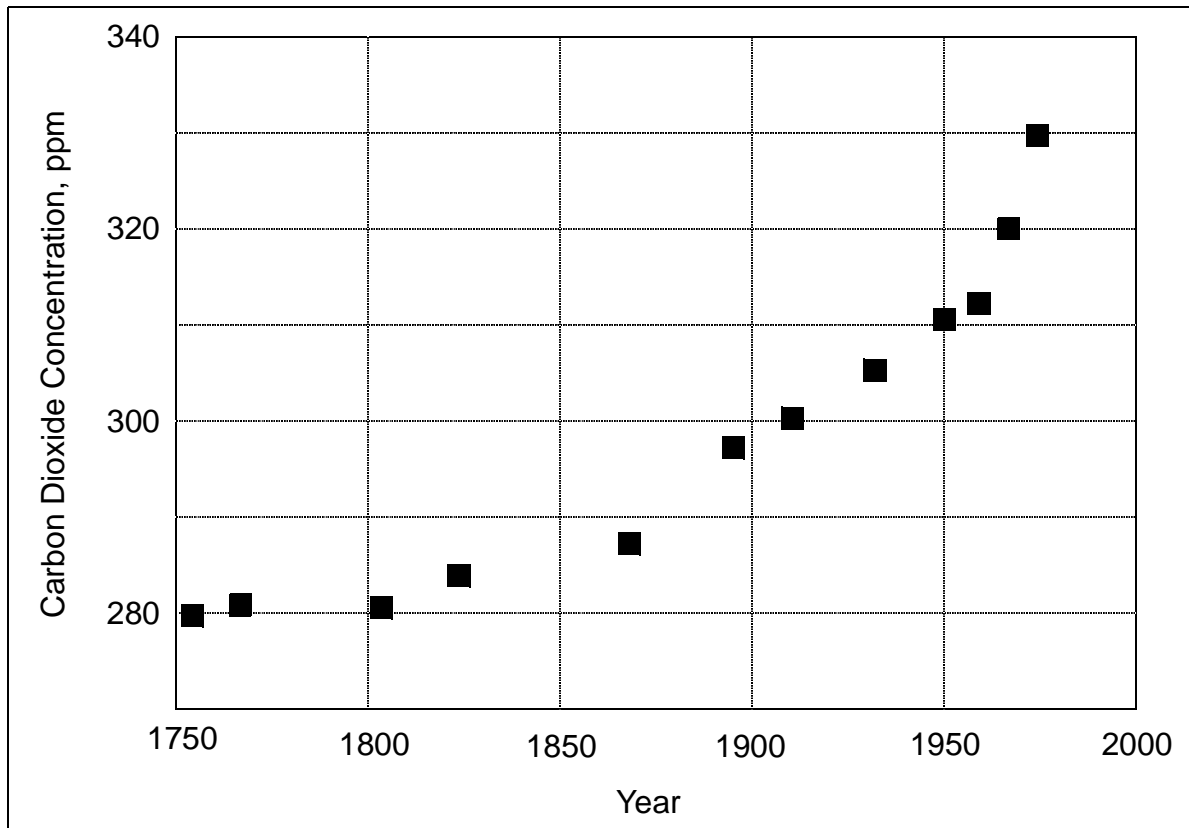


Figure 5-4, Atmospheric CO₂ Concentrations Inferred From Glacial Ice Formed During the Last 200 Years, Neftel et al, Nature, vol 315

5.5.4 A Sustainable Economy

The above examples of successful lead abatement and the inability to reverse the generation of CO₂ by fossil fuel combustion have raised questions about the long term health of the world's economy. People have expressed this concern in the term "sustainable economy." To some, it means "no growth," while to others it means "an expanding economy to provide jobs for everyone." Another person might indicate that current decisions should not impair the prospects for maintaining or improving future living standards. Each person has a definition which depends upon their own circumstances and their view of the world. Ayres* has been even more specific with regard to the environment, indicating that to attain a sustainable economy there should be:

1. No anthropogenic change in climate.

* Robert U. Ayres, *op. cit.*; see page 7-1.

2. No net increase in the acidity of the environment.
3. No net accumulation of toxic heavy metals, radioactive isotopes, or long-lived halogenated chemicals in soils or sediments.
4. No net withdrawal of ground water.
5. No net loss of topsoil.
6. No further net loss of wetlands, old-growth forests, or biological diversity.

Maintaining these environmental factors will necessitate a particular diligence in controlling the material flows required for energy production and for product creation and use.

Problems:

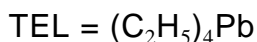
1. Tetraethyl lead, TEL, additions to gasoline were discovered in the 1920s to have beneficial effects upon performance of internal combustion engines. As a result the usage of this additive increased up until the negative environmental contributions were realized in the mid - 1970s, see Fig. 5-3. Given the following data table illustrating the amount of lead used to produce tetraethyl lead-containing gasoline in the U.S., and assuming a smooth curve in between data points:

Table 1: Metric Tons Pb in TEL

Year	Tons Pb inTEL	Year	Tons Pb inTEL	Year	Tons Pb inTEL
1940	30,000	1970	127,300	1985	36,400
1950	49,000	1975	150,000		
1960	82,700	1980	72,700		

a. Estimate the total amount of Pb used in motor fuels in the U.S. to date.

b. Assuming that the bulk (estimated at 80 % of total; the remaining 20 % remains within the vehicle or lubricants) of the Pb in gasoline remains within 100 meters of the roadways, that the roadside ecosystem in the U.S. is about 3×10^7 hectares, and that the mean value of Pb in uncontaminated soils is about 20 ppm, compute the mean value of Pb in the roadside ecosystem which is due to TEL emissions.



EP Toxicity, Max Pb = 5 Mg / Liter = 5 ppm

MCL, Maximum contamination level in water = 0.05 mg / liter = 0.05 ppm

5.5 Material Flow in the Production of Steel

5.5.1 Introduction

Iron (Fe) based metallic materials have been and will continue to be the dominant metallic material because of their low cost, abundance in the earth's crust, and because of their excellent physical and mechanical properties. The low cost follows somewhat from iron's abundance in the earth's crust. In addition, iron ore bodies are typically much richer in Fe than other metallic ores are in their primary metals. For example, compare copper (Cu) and Fe:

Cu: 150-200 metric tons ore → 1 metric ton Cu
 Fe: 2-4 metric tons ore → 1 metric ton Fe

The importance of iron and iron-based products can be seen in Table 5-1, below, showing the 1997 world production of primary metals and the 1996 world production of castings.

Table 7-2: World and U.S. Production Statistics of Primary Metals and Castings (in millions of metric tons)

Primary Metals*			Castings**		
Metal	World	U.S.	Metal	World	U.S.
Steel (97)	792.8	128.5	Cast Iron and Steel	59.6	11.7
Aluminum (96)	20.7	3.6	Aluminum base	6.37	1.64
Copper (97)	10.8	1.7	Copper base	1.03	0.31
Zinc (97)	7.7	0.45	Zinc base	0.81	0.37
Magnesium (96)	0.34	0.13	Magnesium base	0.05	0.03
Percent Ferrous	95.2	95.6		88	83

*Data from *Metal Statistics* 1998, for the years 1996 & 1997, American Metal Market.

**Data from *Modern Casting*, Dec. 1997, American Foundrymen's Society.

The largest share of primary metals production goes into the generation of wrought products, products formed by rolling, extruding, or forging as-cast billets, bars, plates or ingots. Castings are defined here as metal parts which are cast-to-shape (which receive no metal working components). It can be seen from Table 5-1 that ferrous products overwhelm all other primary metals or castings produced in the world and in the U.S.

Use of Fe-based Materials in Automobiles

An excellent example of the use and continued use of Fe-based metals is the amount used in automobiles in the past and in the more recent era of lighter-weight, smaller vehicles. The data given in Table 5-2 represent the weight

percentages of the most common materials used to produce Ford Motor Company products in 1975 ,1990 and projected to 2000.

Table 7-3: Change in Materials Content of Ford Automobiles*

Material	Weight Percent		
	1975	1990	2000
Steel/Cast Iron (CI)	76	58	69.2
High Strength Steel	2.5	11.5	(CI = 10.3)
Aluminum	2	6	7.3
Plastics	4	10.5	10.7

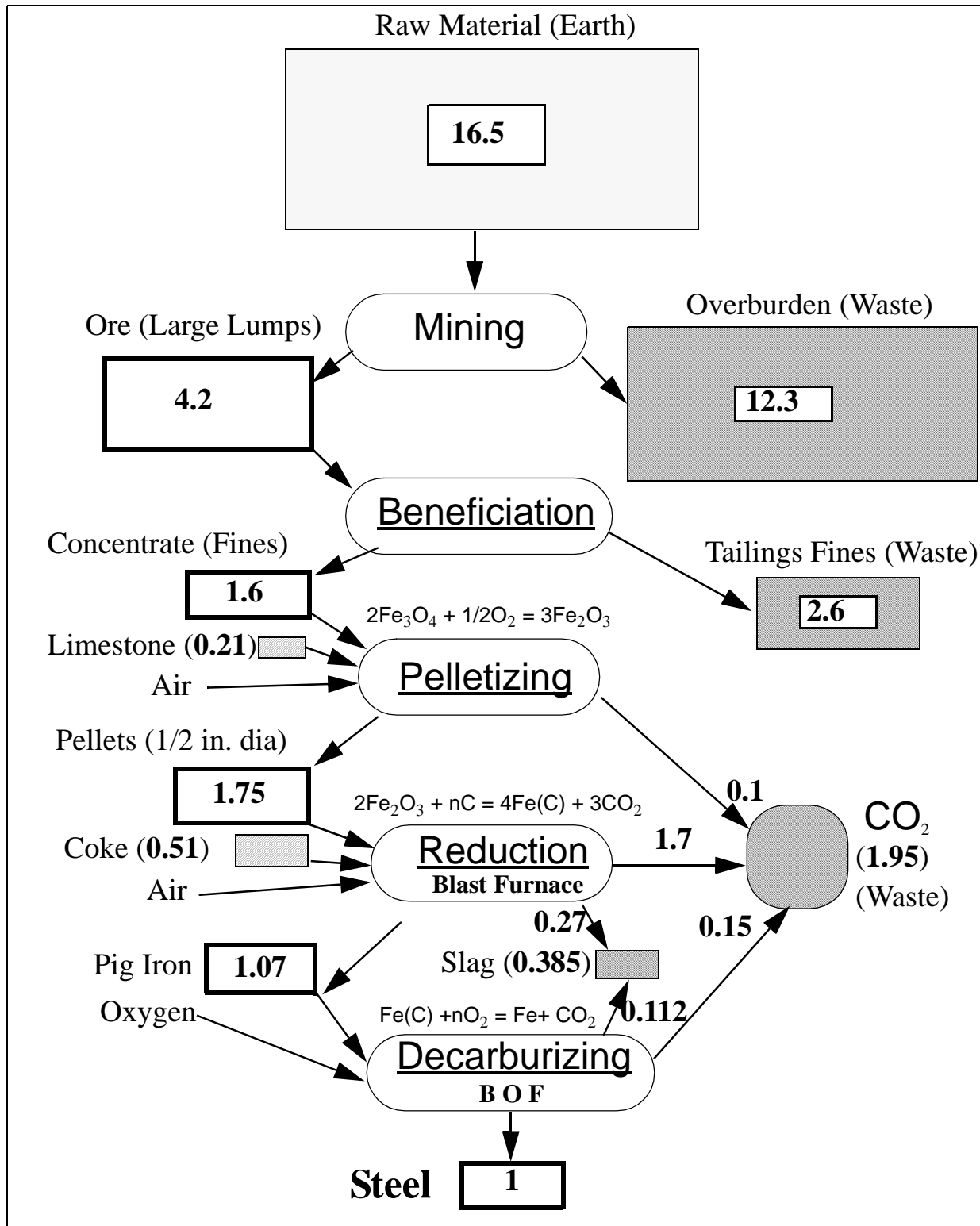
*From N. A. Gjostein, Ford Motor Company

It is interesting to note that while the percentage of aluminum and plastics have both increased, the total amount of Fe-based material present has decreased only from 78.5 wt. percent to 69.5 wt. percent in 1990 and then only to 69.2 % in 2000. Thus the iron content of the average automobile still is more than two-thirds the weight of the vehicle, or about 2000 lbs. (1 short ton) for the average 3000 lb. vehicle. The majority of the iron-based material present is steel, and since the cast iron present is produced primarily from scrap steel, it is clear that steel is the dominant material used to produce automobiles today and will likely continue in the near future.

5.5.2 Overview of Steel Production

Steel is basically an alloy of iron (Fe) and carbon (C), with C present in amounts usually less than 0.8 wt. pct. A flow diagram for the production of steel, together with the physical and chemical changes accompanying the iron-containing material are illustrated in Figure 5-5 for each unit operation in the steel making process (Mining, Beneficiation, Pelletizing, Reduction in Blast Furnace, Decarburization in the Basic Oxygen Furnace (BOF)) . The changes accompanying each unit operation require significant inputs of energy and/or other materials, the most important of which are shown in Fig 5-5. The chemical reactions described for the Blast Furnace (reduction of Fe_2O_3) and the Basic Oxygen Furnace (decarburization of hot pig iron) both involve oxidation of carbon to produce CO_2 , an exothermic reaction which is the major heat source for the reactions. Figure 7 - 5 is constructed so that the weight in metric tons of materials needed to produce one metric ton of steel are indicated (numbers in the figure), and the areas are scaled on a wt fraction basis to the weight of steel produced. Note for example that the area representing the raw material is approximately 16.5 times the area of the one ton of steel. In addition the amounts of materials released as waste or by-products is also scaled to the area represented by steel. Some of the details of the concentrations of critical materials in the diagram of Fig. 5-5 are given in the material to follow.

Figure 5- 5 Material Flow Diagram For Steel Production
(Numbers in metric tons)



5.5.3 Mass Balances in Unit Operations: Calculations and Problems

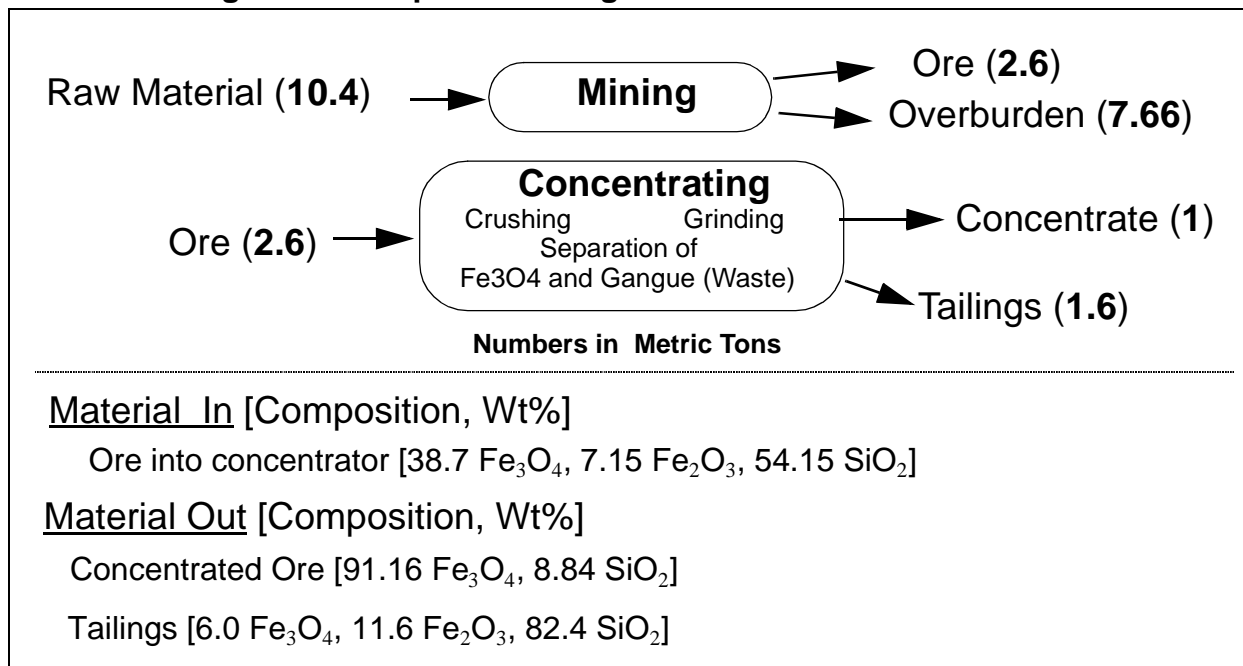
Four of the unit operations described for the production of steel are shown in the following diagrams, Figs. 5-6 to 5-9. Each diagram includes the mass (**bold numbers in metric tons**) into the process and the mass out, together with (in most cases) the concentration of species into and out of the process. It is important to emphasize that these mass balances are simplified a great deal by considering only the essential features of each process. Typical mass balances are in general much more complicated. However, the processes shown are sufficient to demonstrate the process and give “ball park” ideas of material amounts. Each student should study these diagrams in the natural way, as presented:

- First: Mining and Concentrating
- Second: Pelletizing
- Third: Production of Pig Iron in a Blast Furnace
- Fourth: Production of Steel in a Basic Oxygen Furnace

Mining and Concentrating, Figure 5-6

It is important to understand that the iron ore concentrate, the final product, contains some silica. An ideal ore would contain only the magnetite (Fe_3O_4), a result achievable only by spending a much larger amount of energy (and \$) in processing. A cost effective concentrate requires the presence of some of the impurity SiO_2 . By the same token, the tailings (or waste product) will contain a significant amount of iron.

Figure 5-6 Simplified Mining and Beneficiation Mass Balances



Example Calculation:

How much Fe in wt. pct. is disposed of in tailings ponds? This requires first determining the wt. fraction of Fe in Fe_2O_3 and Fe_3O_4 .

$$\text{Wt. Fract. Fe (Fe}_2\text{O}_3) = \frac{2 \times \text{At. wt. Fe}}{2 \times \text{At. wt. Fe} + 3 \text{ At. wt. O}} = \frac{2 \times 55.85}{2 \times 55.85 + 3 \times 16.01} = \frac{111.7}{159.73} = 0.699$$

and

$$\text{Wt. Fract. Fe (Fe}_3\text{O}_4) = \frac{3 \times 55.85}{3 \times 55.85 + 4 \times 16.01} = \frac{167.55}{231.59} = 0.723.$$

Using the concentrations given then in Figure 5-6,

$$\text{Wt.\% Fe in Tailings} = 6 \times .723 + 11.6 \times .699 = 4.338 + 8.108 = 12.446\%.$$

Perhaps in many years the tailings pond will become an ore body. However, this is not economical at this time.

Problem: Beneficiation

1. Determine the concentration (wt. pct.) iron in the ore and concentrate.

Pelletizing (High Temperature Sintering), Figure 5-7

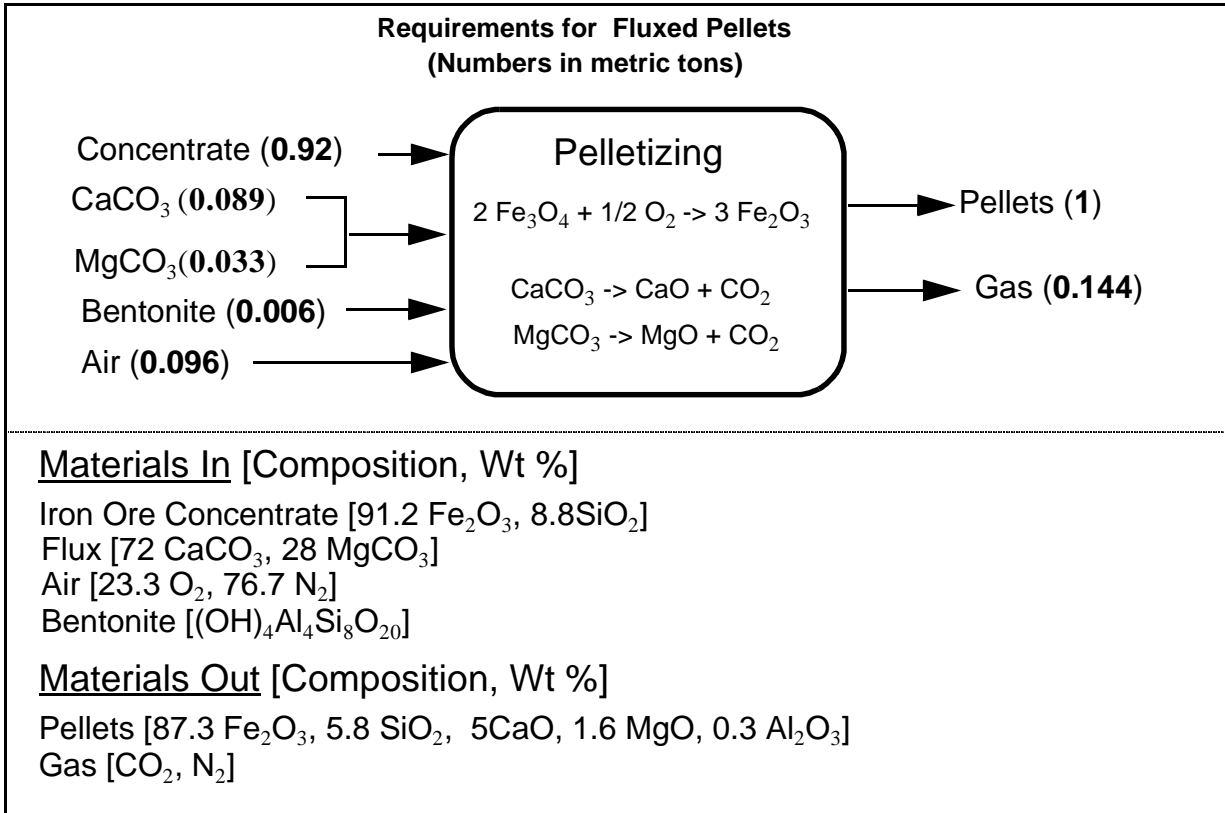
The mass balance shown in Figure 5-7 illustrates the production of what is called a fluxed pellet. Instead of adding the flux to the blast furnace, it is incorporated into the pellets. The purpose of the flux is to produce slag in the blast furnace, a liquid layer formed on the surface of the pig iron which is effective in removing certain impurities. Flux materials are CaCO_3 and MgCO_3 . The bentonite is added to aid in producing strong bonds during the heat of pelletizing. The product is a pellet which will not crush during transportation or as a burden in the blast furnace.

Example Calculation

The limestone (CaCO_3) and dolomite (MgCO_3) are calcined (CO_2 is driven off) during pelletizing. Determine the weight of CO_2 generated during production of one ton of pellets. Atomic weights: Ca-40.08; Mg-24.32; O-16; C-12.01.

$$\begin{aligned} \text{Wt. CO}_2 &= 178 \text{ lb.} \left(\frac{\text{At. wt. CO}_2}{\text{At. wt. CaCO}_3} \right) + 67 \left(\frac{\text{At. wt. CO}_2}{\text{At. wt. MgCO}_3} \right) \\ &= 178 \left(\frac{44.01}{100.09} \right) + 67 \left(\frac{44.01}{84.33} \right) = 112.96 \text{ lb.} \end{aligned}$$

Figure 5- 7 Simplified Pelletizing Materials Balance



Problems: Pelletizing Iron Ore

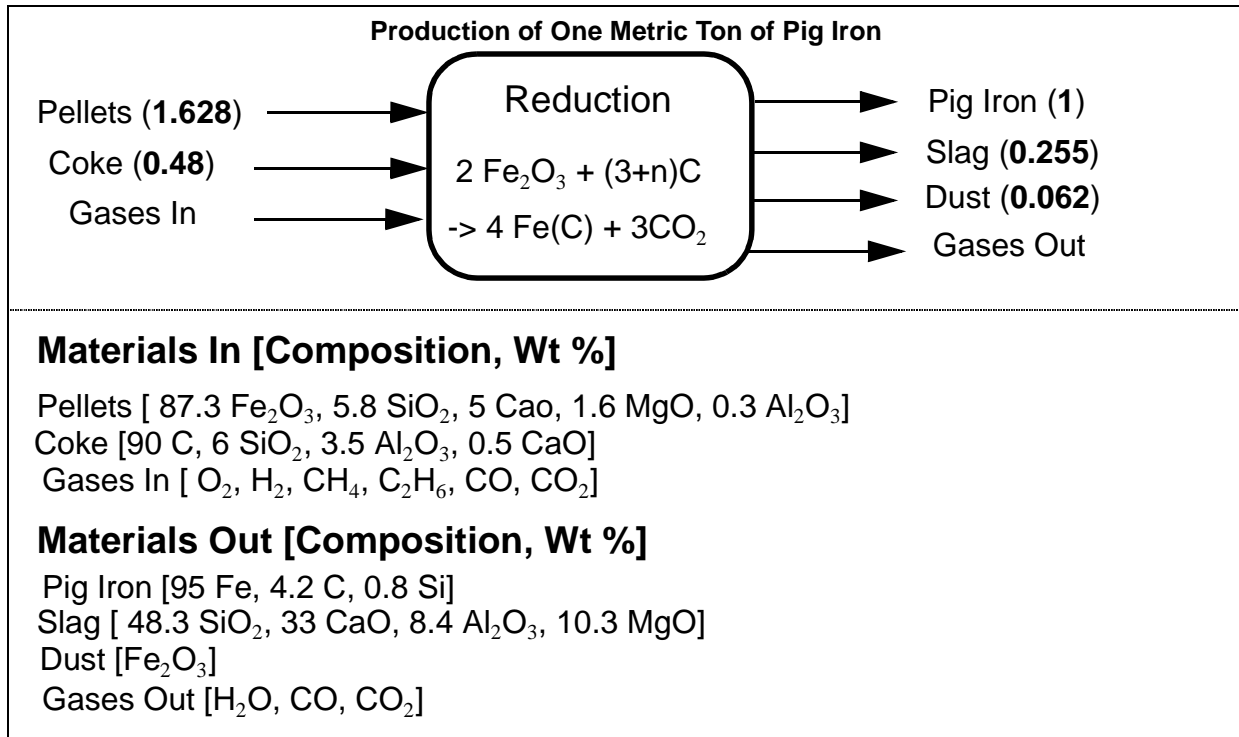
1. Compute the Fe concentration in the pellet.
2. Determine the amount of O₂ and air needed to oxidize the Fe₃O₄ in the 0.92 Metric Tons of concentrate. Air = 23.11 wt.pct. O, 20.99 volume pct. O.
3. A mine produces about 4 million metric tons of fluxed pellets per year and thus creates a significant amount of the greenhouse gas, CO₂. Compare the amount of CO₂ generated here to the amount generated per year by a 1000 MWe coal-fired power plant. (Assume that a 1000 MWe power plant uses 365 tons of coal, @85% C, per hour) Which is greater?

Reduction --- Blast Furnace, Figure 7 - 8

The blast furnace is a complex chemical reaction chamber in which hot gases together with a large amount of coke accomplish the reduction of Fe₂O₃ to hot metal containing a large quantity of carbon. Input gases include oxygen and coke oven gas, a complex mix of methane, hydrogen, carbon monoxide, and other volatiles. The countercurrent nature of the process results in significant quantities of iron going into dust as Fe₂O₃, a product which may be recovered and sintered to produce a size and

shape compatible with recharging into the blast furnace.

Figure 5- 8 Simplified Blast Furnace Materials Balance



Example Calculation

Given the compositions and amounts of materials shown going into the blast furnace, verify that the slag quantity of 0.255 tons per ton of pig iron and the composition shown are accurate.

Assuming the slag comes from the non-ferrous components of the pellets and the coke, then

$$\text{Wt. Slag} = 1.628 (.127) + 0.48 (0.1) = 0.207 + 0.048 \cong 0.255 \text{ metric ton}$$

Composition of slag:

$$\text{Wt. Pct. SiO}_2 = 100 \times \frac{3256(.058) + 960(.06)}{510} = \frac{188.8 + 57.6}{510} \times 100 = 48.3$$

$$\text{Wt. Pct. CaO} = 100 \times \frac{3256(.05) + 960(.605)}{510} = \frac{162.8 + \dots}{510} \times 100 = 32.8$$

etc.

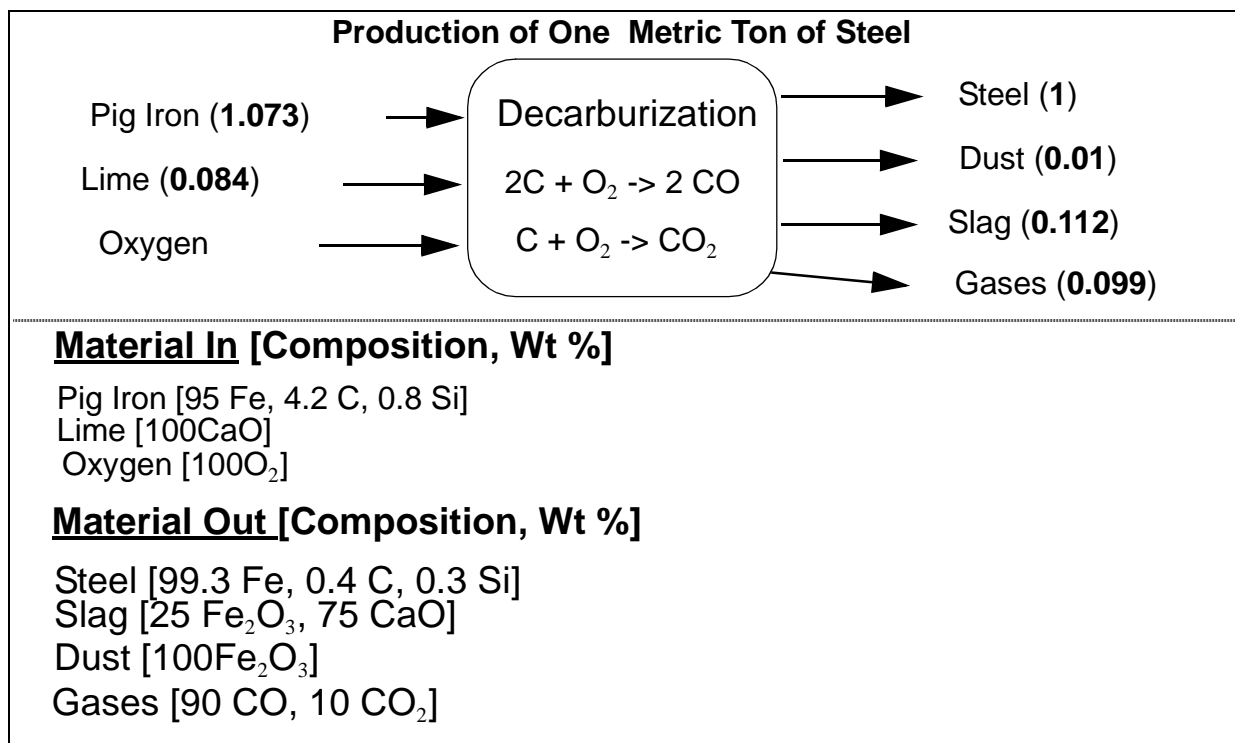
Problems: Blast Furnace

1. Using the inputs and outputs of Fig. 5-8, verify that the amount of Fe entering as pellets is equivalent to that exiting as pig iron and dust.
2. Estimate the amount of C needed to reduce the Fe_2O_3 in the 1.628 tons of pellets going into the blast furnace and that needed to saturate 1 ton of pig iron. Compare the result with the amount of coke input.

Decarburization of Steel—Basic Oxygen Furnace (BOF), Figure 5-9

The Basic Oxygen Furnace (BOF) is a refining furnace whose primary function is to decarburize the pig iron from the blast furnace. In this process, the heat needed is supplied by the reaction of oxygen with the various constituents of the charge (mainly carbon in the pig iron). A typical BOF charge will have a mix of 70% hot metal (pig iron at 2400-2450°F) and 30% cold steel scrap, which when blown with oxygen will raise the temperature of the final steel product to ~3000°F. Again, as in the blast furnace, lime is added to generate the necessary slag, which in this case will contain a significant quantity of iron, a quantity which is recovered using the BOF slag as a flux material in blast furnace burdens not using fluxed pellets. Figure 5-9 illustrates a simplified materials balance for a BOF operation in which no scrap steel is used. This is done only to simplify the calculations which follow, and is not meant to represent a typical BOF charge.

Figure 5- 9 Simplified (B O F) Materials Balance



Problems: Steelmaking with BOF

1. Given the chemical analyses of the pig iron, the resulting steel, and the exhaust gas and dust,
 - (a) Compute the amount of oxygen needed in Figure 5-9.
 - (b) Verify (to the nearest pound) that the iron balance in Fig. 5-9 is correct.

5.5.4 Processing Costs of Unit Operations

The processing costs of the unit operations can be broken broadly into three categories:

1. Material costs
2. Energy costs
3. Other (capital, labor, taxes, insurance)

Data from “The Competitive Status of the U.S. Steel Industry” (The National Academy Press, 1985) summarizes these items for each of the unit operations considered here. Figure 5-10 summarizes the costs for each process in the above three categories, together with the cost of producing steel by electric arc furnace (EAF) from steel scrap (~1985 data). While the costs currently might be slightly different than shown in Fig. 5-10, the relative amounts of the three categories remain the same.

It is interesting to note in Fig. 5-10 that the unit cost of steel produced in EAF from steel scrap is approximately 77% of the cost of “new” steel, that processed from iron ore. This large difference in cost has spawned many mini-mills, steel processing facilities that melt only scrap, usually in electric arc (EA) furnaces. The large quantity of scrap available* allows the mini-mills to compete very successfully with the much larger integrated mills which operate blast furnaces.

Several sources of scrap provide input to EA F furnaces, including:

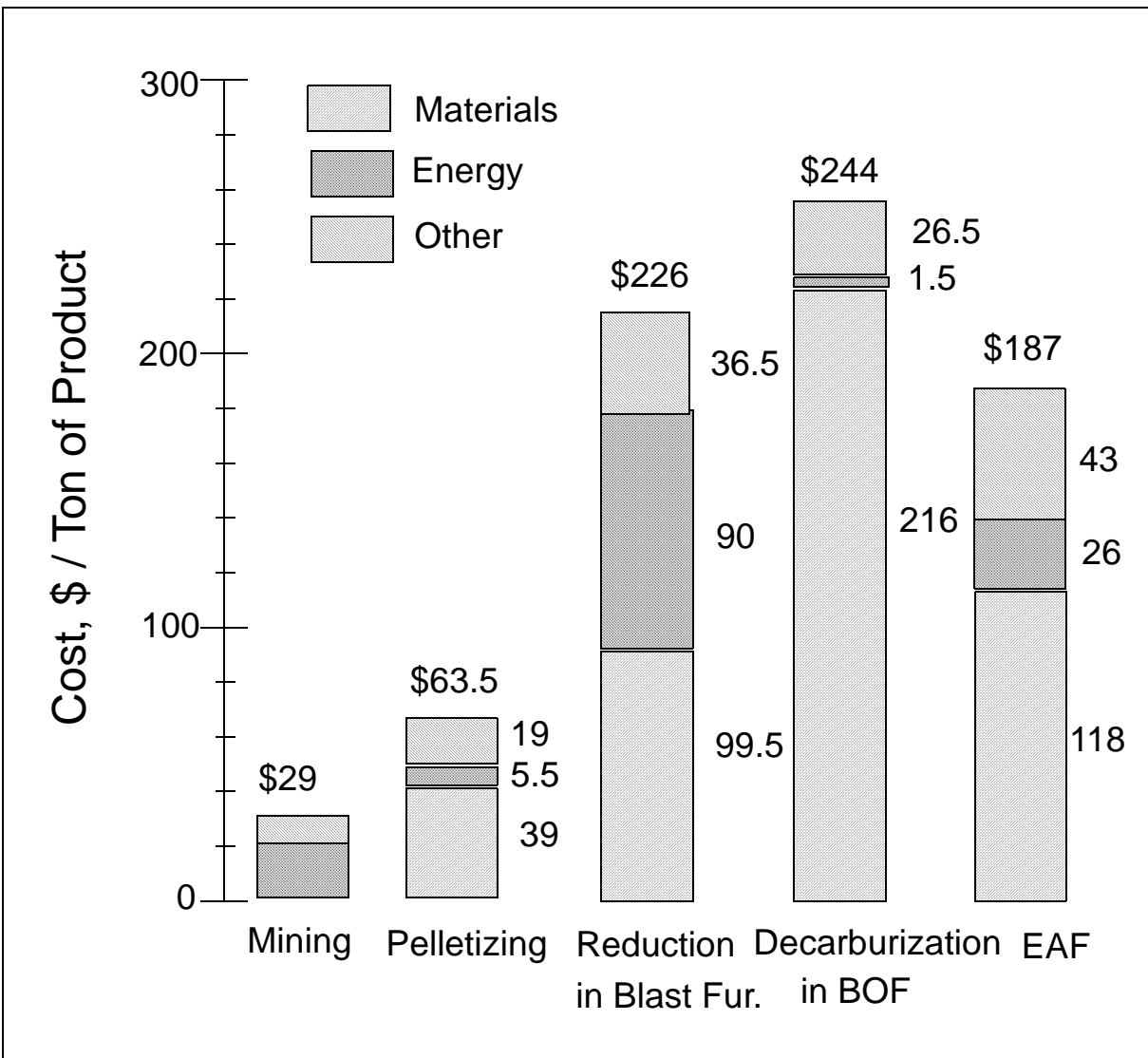
1. Home scrap—croppings from within the steel mill
2. Prompt industrial scrap—trimmings returned by steel users
3. Dormant scrap—materials collected and processed by dealers

Home and prompt industrial scrap are sometimes called “new” scrap because they have not been used as a product. Dormant scrap is most often material recycled after use, such as old shredded automobiles, worn rail, railroad wheels, structural steel salvaged from buildings, etc.

* It has been estimated that in the U.S. alone, approximately 800 million tons of steel scrap *is available* for recycling through EAF facilities or through iron foundries. It should be noted that this large amount of scrap is approximately equivalent to the annual world production of steel, and approximately 3 times the 270 million metric tons of scrap steel reprocessed to steel in the world in 1990.

It is instructive to consider the flow of steel to the automotive industry, to the consumer, and finally back to steel producers as scrap. According to the 1995 annual Statistical Report of the AISI, 13.29 million metric tons of steel were shipped to the automotive markets (which is the largest single customer for steel suppliers in the U.S.). At one short ton per vehicle, this translates to ~14.6 million vehicles produced domestically. Eventually these vehicles will be returned to furnaces as scrap to be recycled into new products.

Figure 5-10
Unit Operation Costs for Steel Processing



From "The Competitive Status of the U.S. Steel Industry" (The National Academy Press, 1985)
 Energy costs include all contributions from coal, coke, fuel oil, natural gas, blast furnace gas, electricity

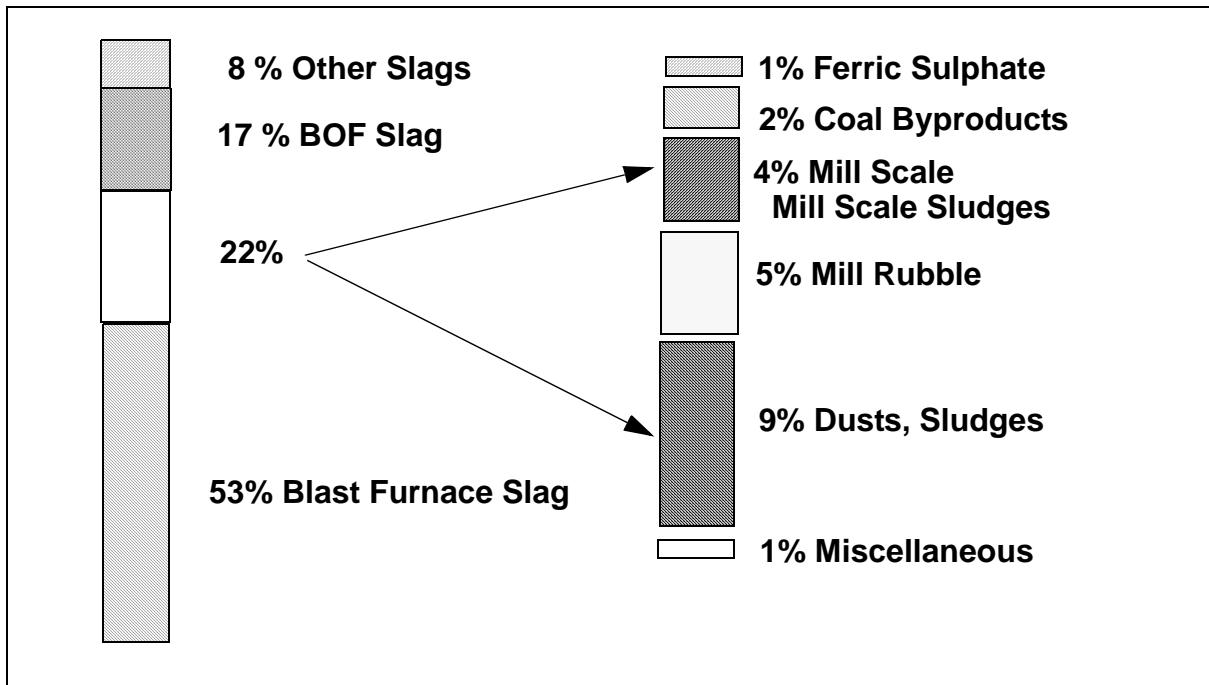
5.5.6 Environmental Considerations and Reuse of Steelmaking By-products

Each unit operation has associated with it significant environmental concerns. Discharges from these unit operations include solids, liquids, gases and heat. Many of these “waste” products are recycled for their energy or mass content. Examples of these include:

1. Fe₂O₃ dust from Basic Oxygen Furnace, BOF, and blast furnace, BF: Sintered and returned to BF.
2. Slag from blast furnace: Road fill, construction uses.
3. Slag from BOF: Flux for BF, Fe value (~20%) recovered.
4. Mill scale (Fe₂O₃) from hot mill: Sintered and returned to BF or BOF.
5. Hot BF gases preheat blast air.
6. Hot BF and BOF gases used to heat buildings.
7. Coke oven gas used as fuel in BF.

All of these processes are constantly monitored to minimize land, water and air pollution which accompanies the production of steel. Figure 5-11 is a schematic of the breakdown of solid waste materials and their approximate percentages.

Figure 5-11
Breakdown of the Waste Materials by Location in Steel Production



5.6 Material Flow in the Production of Copper

5.6.1 Introduction

Copper (Cu) is an excellent conductor of electricity and has excellent corrosion resistance. Used in a broad range of alloys, it is the basis for the production of brasses (Zinc containing alloys) and bronzes (Tin containing alloys). Annual output of copper from U.S. mines is about 1.5 million tons per year, about 1 - 2 percent of the annual output of steel. As indicated in the introduction to material flow in the production of steel, copper ores are much less rich than iron ores resulting in a much more extensive concentrating process for copper.

5.6.2 Overview of Copper Production

Copper is found in the forms of sulfides, oxides, carbonates and as a native metal; the native metal is found only in small quantities, most notably in the Upper Peninsula of Michigan. Amounts of copper present in the ores which are currently being mined commercially vary from as little as 0.2 wt. % to as high as 4 wt %. The amount of copper and the form that it takes determines the processing requirements needed to separate and refine the copper. This section will outline the material flow of copper from an ore body containing the sulfide form, Cu_2S (chalcocite), a process modelled after the material flow from an underground mining operation.

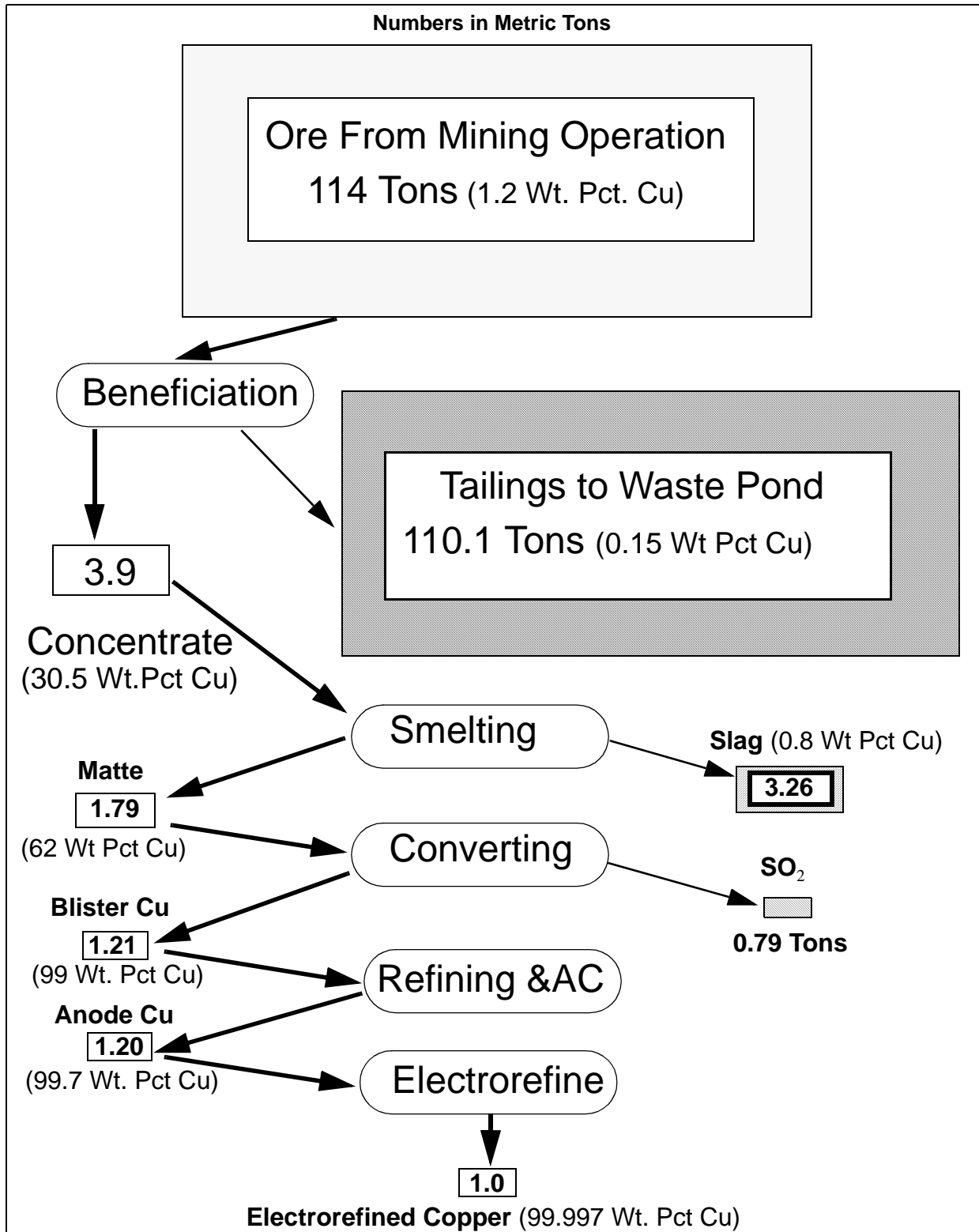
The basic unit operations required to produce a high purity electrical grade of copper from this underground mine are listed below and described in a diagram in Fig. 7 - 12.

Unit Operations

1. Mining - Removal of Ore in Seams (1.2 wt Pct Cu) Leaving Waste Rock Underground
2. Beneficiation - Production of Concentrate containing 30.5 wt. pct Copper, Discarding Waste Rock in Tailings Pond
3. Smelting - Production of Matte (62.5 wt pct Copper) in a coal - fired reverberatory furnace, Discarding Slag to Dump and SO_2 Gas into the Atmosphere
4. Converting - Production of Blister Copper (99 wt. pct Copper) with release of SO_2 gas to Atmosphere and Slag Recycled to the Reverberatory Smelting Furnace.
5. Fire Refining - Deoxidizing the Blister Copper to Produce Anode Copper (99.7 wt. Pct Copper)
6. Anode Casting and Electrorefining - Produce Anode Shape, Electrorefine to Produce 99.997 Wt. Pct Copper. Send Slimes to Recover Precious Metals (Ag, Au, Pt, etc.)

It can be seen in Fig. 5-12 that the amounts of materials discarded is much larger for copper production than for steel production. As in Fig. 5-5, the numbers refer to the estimated tons of materials required in various unit operations to produce 1 Ton of Electrorefined Copper, numbers proportional to the areas of the boxes shown. It should be noted that Fig 5-12 is a very much simplified diagram, with only the Cu containing material and major waste materials shown.

Figure 5- 12 Material Flow Diagram for Copper Production



5.6.3 A detailed Look at the Mass Balance for the Converting Unit Operation

As is the situation depicted in Figs 5-6 through 5-9 for the Unit Operations required in the production of steel, each one of the unit operations depicted in Fig 5-12 requires a very detailed description of the mass inputs and outputs as well as their compositions. The complexity of the situation is illustrated for the converting reaction in Fig. 5-13. The reader will keep in mind that this too is a much simpler representation than in reality. The other unit operations are equally complex.

Figure 5- 13 Schematic Daily Mass Balance For Converter (Metric Tons)

INPUTS		Reactions	OUTPUTS	
Material	Tons / Day		Material	Tons / Day
1. Matte	335	1. $\text{Cu}_2\text{S} + \text{O}_2 \rightarrow 2\text{Cu} + \text{SO}_2$	1. Blister Copper	227
2. Air	468	2. $\text{FeS} + 3/2 \text{O}_2 \rightarrow \text{SO}_2 + \text{FeO}$	2. SO2 Emission	153
3. Reverb. Slag	68	3. $3\text{FeS} + \text{SO}_2 \rightarrow \text{Fe}_3\text{O}_4 + 3\text{SO}_2$	3. Converter Slag	150
4. Anode Scrap	18		4. Other Air Emissios (N2, Dust, Excess Air)	394
5. Other Secondaries	53			

Material In [Composition, Wt. Pct]

1. Matte [62 Cu, 12 Fe, 22 S]
2. Air [20 O, 80 N]
3. Reverb slag [0.8 Cu, 43.1 SiO₂, 13.7 Al₂O₃, 14.6 Fe, 20 CaCO₃, 3.4 MgO]
4. Anode Scrap [99.7 Cu, 0.25 O]
5. Other Secondaries [High Percentage Cu (Variable)]

Material Out [Composition, Wt. Pct]

1. Blister Copper [99 Cu, 0.6 O, ?]
2. Gaseous SO₂ [50S, 50O]
3. Converter Slag [5 Cu, 2 S, 34 Fe, 10 Al₂O₃, 12 CaO, 2 MgO, 26 SiO₂]
4. Converter Dust [75 Cu, ?]

5.6.4 Scrap and Secondary Production of Copper

Copper containing scrap is the major scrap category on the non-ferrous side. For example about a third of the feed that goes into the production of pure copper metal produced in the United States is scrap. In addition, in the year 1997, 1,157,300 metric tons of “new” or “prompt” copper-base scrap (including copper and all alloys) was processed in the U.S. while 564,600 tons of “old” or “dormant” scrap was recovered. The total U.S. consumption of scrap copper and copper alloys in the year 1997 was 1,721,900 metric tons, which is only a little less than the amount produced by U.S. mines (1,920,000 metric tons) in 1996. **(Metal Statistics, 1998, 90 th Edition)**

5.6.5 Environmental Considerations and Reuse of Copper Production By-Products

The production of copper and its alloys involves environmental concerns, some of which are indicated below:

1. Examination of Fig. 5-12 shows that a huge quantity of solid waste tailings are generated (records indicate ~110 tons of waste per ton of copper produced). Fortunately this waste is not particularly toxic, requiring only large areas in which to deposit. Slag production is also significant. Fig. 5-12 shows a ratio of slag to Cu of about 3 to 1 by weight, which converts to about 10 to 1 by volume. Again this is not generally a toxic material, and can be used in other ways (road fill,etc.).
2. Smelters which convert copper sulfide into copper necessarily generate a significant amount of SO₂ and CO₂, the SO₂ coming from the smelting and converting operations (See Fig. 5-13) and the CO₂ coming from the roasting of limestone (flux for slagging purposes) and the combustion of fuels. Sulfur dioxide which is vented out of the stacks contributes significantly to the generation of conditions which can produce acid rain. Modern smelters, however, recover the SO₂ by producing a by-product of sulfuric acid, H₂SO₄. The generation of CO₂ in combustion and roasting contributes to the increasing amounts of greenhouse gases in the atmosphere. However this contribution is small compared to that generated by steel and cement production. Other potential pollutants accompanying the production of Cu include emission of Hg, Pb, Cd, etc. These elements would normally exit via the stack, but can be recovered with appropriate scrubbing equipment.
3. A particularly serious problem facing U.S. industry in the 1990's is an attempt to mitigate the lead (Pb) pollution problem faced by the plumbing industry due to the leaching of the Pb into the potable water supply. Lead is added to brasses and bronzes for the purpose of improving machinability, a job which it does better than anything else. Efforts to minimize the problem have included the (1) development of Pb-free alloys, (2) study of ways to pre-leach the Pb exposed to the water prior to selling the product, and (3) develop techniques to coat the water-exposed portion of the fixture with a material which does not erode in service thereby preventing the Pb from coming into contact with the water.

Problem:

1. Opportunities for reducing the emission of S to the atmosphere as SO₂ can take the form of production of either elemental S (solid) or Sulfuric Acid (liquid). Assuming both methods of recovering S were used, estimate the volumes of S and/or H₂SO₄ recovered per day from the indicated converting operation.

5.7 Material Flow in the Production of Aluminum

5.7.1 Introduction

Aluminum (Al) ranks second only to the production of iron and steel in the metals markets. In 1995 U.S. industry produced 3.375 million metric tons of primary aluminum. The largest share of the market goes to transportation (27.2%), containers and packaging (~24.1 %), while building and construction (~12.7 %) make up the largest share of the remainder (Aluminum Statistical Review for 1995; The Aluminum Association).

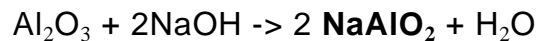
5.7.2 Overview of Primary Aluminum Production

The primary production of Aluminum is a very complex energy intensive process involving several unit operations listed below:

1. Mining an Ore Containing Alumina (Al_2O_3), typically 35-55 wt pct.
2. Separating the alumina from the ore in the **Bayer Process**:

- a. Crushing and Grinding to produce a size fraction in which the alumina can be liberated.

- b. Digestion in Caustic Solution of NaOH at 143-147 °C giving:



The remaining undissolved solids (red mud) is removed.

- c. Seeding with small particles of Alumina Trihydrate ($\text{Al}(\text{OH})_3$) and Slowly Cooled from 145 to 25°C so that the following reaction occurs:

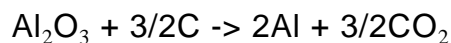


- d. Calcining at 1100°C where the water is driven off:



3. Electrolytic Refining in the Hall Cell

In this energy and material consumption intensive process the alumina is dissolved in molten cryolite (typical composition of $87\text{Na}_3\text{AlF}_6$, 5AlF_3 , and 8CaF_2) at 940-970°C. A high electrical current (~1000 A / ft²) at 6-7 volts is applied between a carbon containing electrode and the molten bath in which the following reaction occurs:

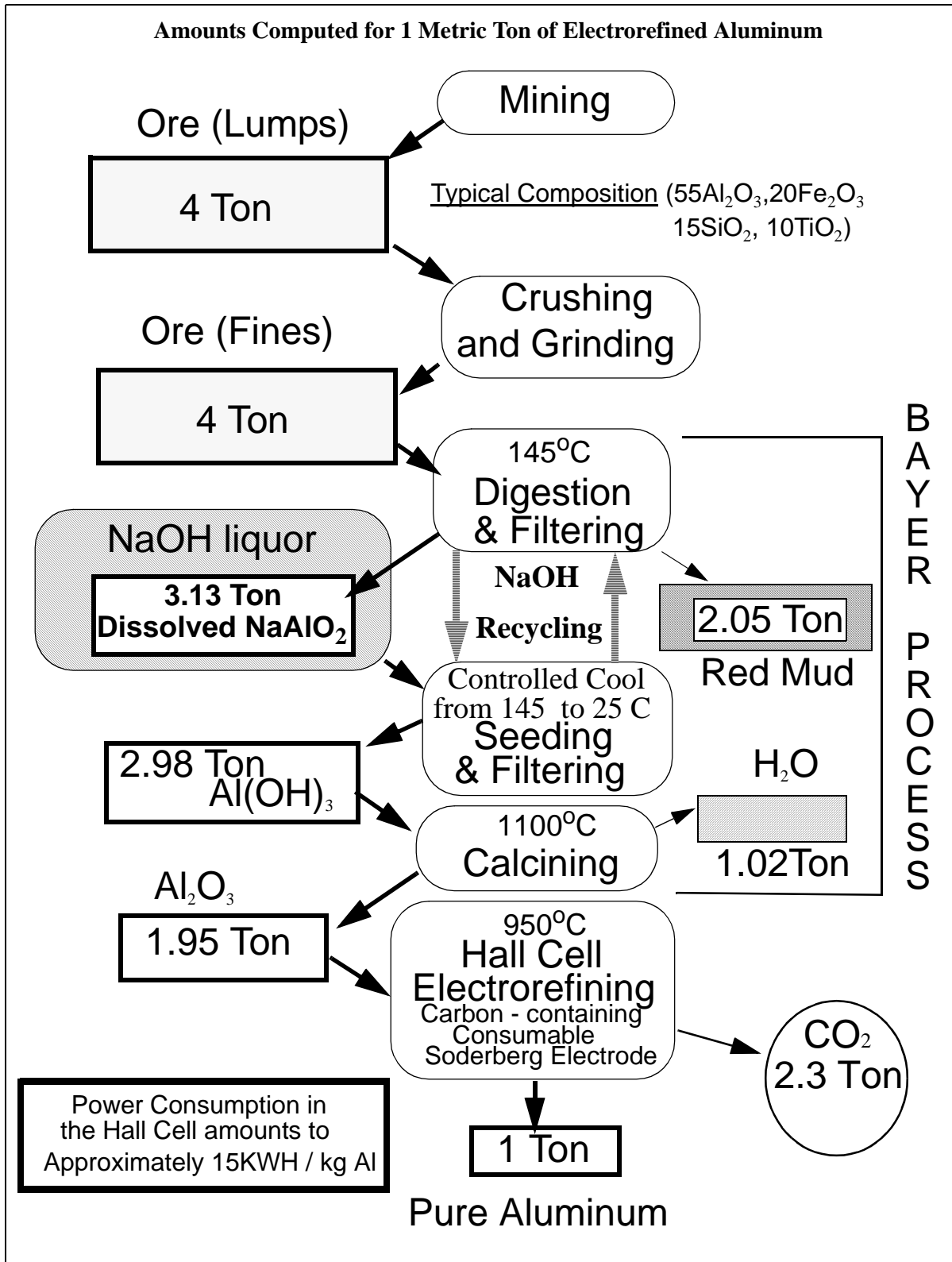


The molten aluminum collects at the bottom of the vessel and the CO_2 exits the system to the atmosphere.

A schematic material flow sheet for aluminum production similar to those for steel and copper is given in Fig. 5-14. Again it is important to realize that the processes are much more involved than what is shown, and that the areas of the outputs are proportional to the weight required at each step to produce one ton of aluminum. It should be noted that the relative amount of waste generated in the process is quite small compared to that in the production of copper, but comparable

to that in steel.

Figure 5-14 Material Flow Diagram For the Production of Aluminum



5.7.3 Scrap and Secondary Production of Aluminum Alloys

Secondary aluminum smelting is a mature industry that relies on a steady flow of scrap from manufacturing industries, military bases, demolition and discarded household goods. In particular, the recycling of used beverage containers (UBC) has become an important source of aluminum for many applications requiring secondary material. In the year 1995, approximately 62.7 billion cans representing 62.2 % of those sold and ~0.92 million metric tons, were recycled in the U.S. This represents about 24% of the amount of primary aluminum produced annually in the U.S.

5.7.4 Environmental Considerations and Reuse of Aluminum Production By-Products

The production of aluminum and its alloys involves environmental concerns, some of which are indicated below:

1. A major concern of the primary aluminum industry is the enormous energy cost to produce this important metal, and many improvements in efficiency have reduced the energy use significantly in the last few years. Considering that the energy to produce primary aluminum is about 20 times that to remelt scrap, it is understandable why the aluminum industry has put such a premium on recycling, particularly UBC.
2. As shown in Fig. 5-14, each ton of primary aluminum produced also requires the production of about 2.3 tons of CO₂, the greenhouse gas. This emission comes from the consumable Soderberg electrodes.
3. The red mud shown in Fig 5-14, a by-product of the Digestion part of the Bayer process, is high enough in iron that it can be used as charge material in an iron blast furnace. Of course, this application only applies where a blast furnace is readily available, a situation which does not usually exist. Consequently most of the red mud is landfilled.

Problem:

1. Assume that all of the ferrous component of domestic automobile production could be replaced by aluminum alloys, a material change which would reduce the weight of an average automobile by 1000 pounds.
 - a. Estimate the annual amount of aluminum needed to maintain the flow of raw material to the domestic auto industry. (This will require an estimate of the annual production of the industry.)
 - b. Assuming that the bulk of the aluminum needed is obtained from primary sources, compute the amount of CO₂ generated per automobile, and annually from the entire industry. How do these amounts compare with that from the current ferrous - based automobiles?
 - c. Comment on the implications for cost comparisons between

ferrous- based and aluminum - based automobiles.

5.8 Material Flow and Energy Requirements in the Production of Portland Cement

5.8.1 Introduction

Like the production of Al, Cu, and Steel, the production of cement involves large quantities of diverse materials, combustion, and high temperatures. Like these metals, the process also results in significant quantities of waste material emitted as gas, or solid. The quantity of cement produced in the U.S. is on the same order by weight as the production of steel. In the year 1993, production of portland cement in the U.S. was approximately 72.7 Million Metric Tons.

5.8.2 Energy Requirements for Cement Production

The energy requirements of a cement kiln are quite large, provided by combustion of powdered coal, some other fuels such as natural gas, fuel oil, or even some waste products from other processes (such as old tires). The theoretical fuel requirement to produce a typical Portland Cement is given as 1.5×10^6 BTU / Ton (1.59 Gigajoules / Ton); actual energy requirements range from 4 - 7 Gigajoules per ton depending on the efficiency of the particular kiln. According to a representative from the Portland Cement Association (January, 1995) the 1994 average energy requirement in the U.S. was ~ 4.3 million BTU per ton (4.56 Gjoule / Ton), the industry having invested significant value into recuperative systems for charging, preheating, etc.

5.8.3 Overview of Portland Cement Production

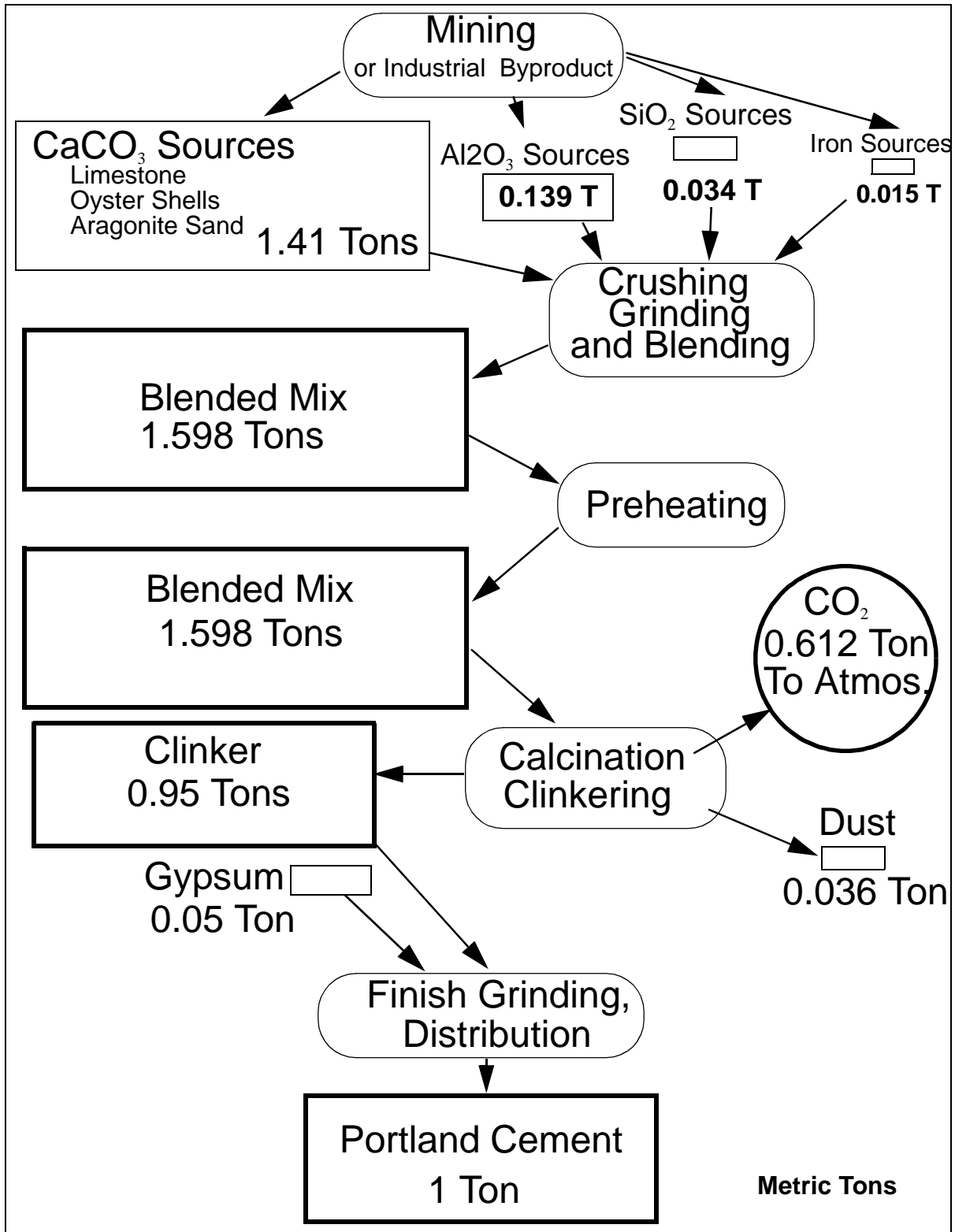
The production of portland cement is also a very complex, energy intensive process in which a large number of materials are brought together for the purpose of creating a useful mix of calcium - containing compounds which when mixed with water creates a useful, strong bond between sand and gravel. Significant steps involved in the production of cement are listed below.

1. Mining (Quarrying) sources of CaCO_3 (Limestone), Al_2O_3 (alumina), SiO_2 (Silica), and sources of iron (Fe_2O_3).
2. Crushing, grinding and blending the quarried material to produce a charge.
3. Preheating the charge .
4. Burning in a Kiln to form a Clinker of Cement. Release of CO_2
5. Add gypsum, finish grinding the clinker, bag for sale.

These steps are illustrated in the material flow diagram of Fig 7 - 15, in which the relative amounts of materials needed to produce one ton of cement are indicated by the sizes of the boxes and the numbers listed. Tonnage information listed was obtained from the U.S. Bureau of Mines Minerals Yearbook, the numbers representing a composite of the entire industry. Individual plants can have large variations in their inputs depending on location, their product mix, etc. This diagram is a very simplified flow diagram intended to give the basic idea of material flow independent of the fuel use. Clearly a significant amount of fuel with its included impurities will contribute to the output of the kiln, and increase the amount

of CO₂ generated as well.

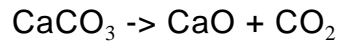
Material Flow Diagram For The Production of Portland Cement



5.8.4 Environmental Concerns in the Production of Portland Cement

The gaseous and solid emissions from the production of portland cement provides some environmental challenges as well as opportunities. Some of these are listed below:

1. The production of the greenhouse gas, CO₂, is an integral part of the process to produce portland cement. Figure 5-15 shows that for every ton of portland cement approximately 0.612 tons of CO₂ are released to the atmosphere as a result of the calcination of the limestone;



In addition to calcination, the combustion of fuel needed in the sintering process releases roughly an equivalent amount of CO₂. Thus for every ton of cement produced, approximately 1.2 tons of CO₂ are released to the atmosphere.

Problem:

Compare the annual contribution of CO₂ to the atmosphere from cement production with that for steel production and primary aluminum production.

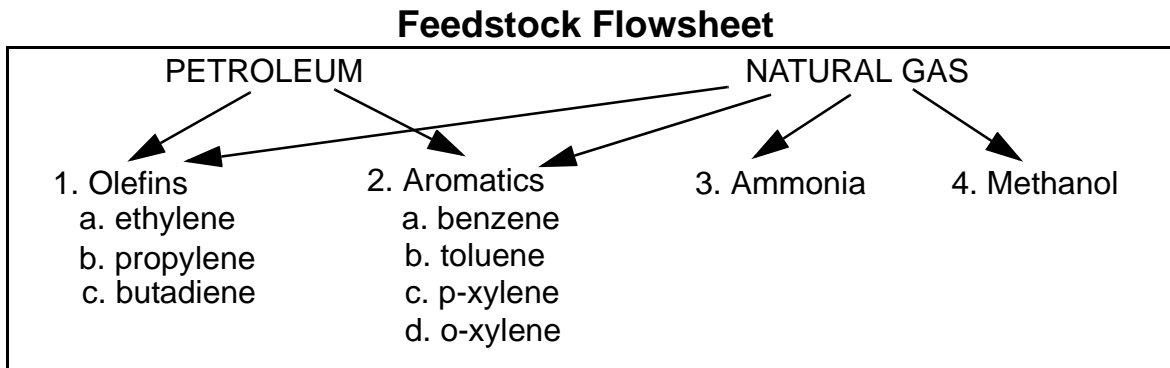
2. Many cement kilns use waste materials as charge and as fuel for sintering. For example, spent foundry sands and fly ash are used as a source of silica, blast furnace slags are used as a source of lime and alumina, and municipal waste and shredded tires make up a significant amount of the fuel used in U.S. cement kilns. Any waste that contains carbon or other combustible material is a potential fuel for these kilns, and many people view them as hazardous waste incinerators. Of course there is the possibility that some hazardous waste could survive the process and either be released up the stack into the atmosphere or could make its way into the dust (note the significant amount of dust created in the process as indicated in Fig. 5-15).
3. In some instances the kiln dust is being used as an agricultural lime and fertilizer, provided of course that there are no hazardous materials present to leach into the soil. In addition, there is interest in kiln dust being used to capture SO₂, HCl and CO₂ in flue gases.

5.9 Material Flow in the Production of Plastics

5.9.1 Introduction

The primary source of feedstock for the production of plastics is derived from petrochemicals (fossil fuels of natural gas and petroleum), or from coal conversion processes which produce coal tars (coke making processes). Agricultural products also provide another source of chemical feedstocks. Coal was once the principal feedstock for chemical production, but in the 1950s it became more economical to obtain most industrial chemicals from petroleum and natural gas (Encyclopedia of Chemical Technology, Volume 10, pg 325, 4th Edition, 1993). As a result, discussion here will be confined to feedstock obtained from petroleum.

The following information was obtained from The Encyclopedia of Chemical Technology, Vol. 10, Edition 4, page 349. "It is convenient to divide the petrochemical industry into two general sectors: (1) olefins and (2) aromatics and their respective derivatives. Olefins are straight or branched-chained unsaturated hydrocarbons, the most important being ethylene, propylene, and butadiene. Aromatics are cyclic unsaturated hydrocarbons, the most important being benzene, toluene, p-xylene, and o-xylene. There are two other large-volume petrochemicals that do not fall easily into either of these two categories: ammonia and methanol. These two products are derived largely from methane (natural gas). These materials are indicated in the Feedstock Flowsheet diagram below:

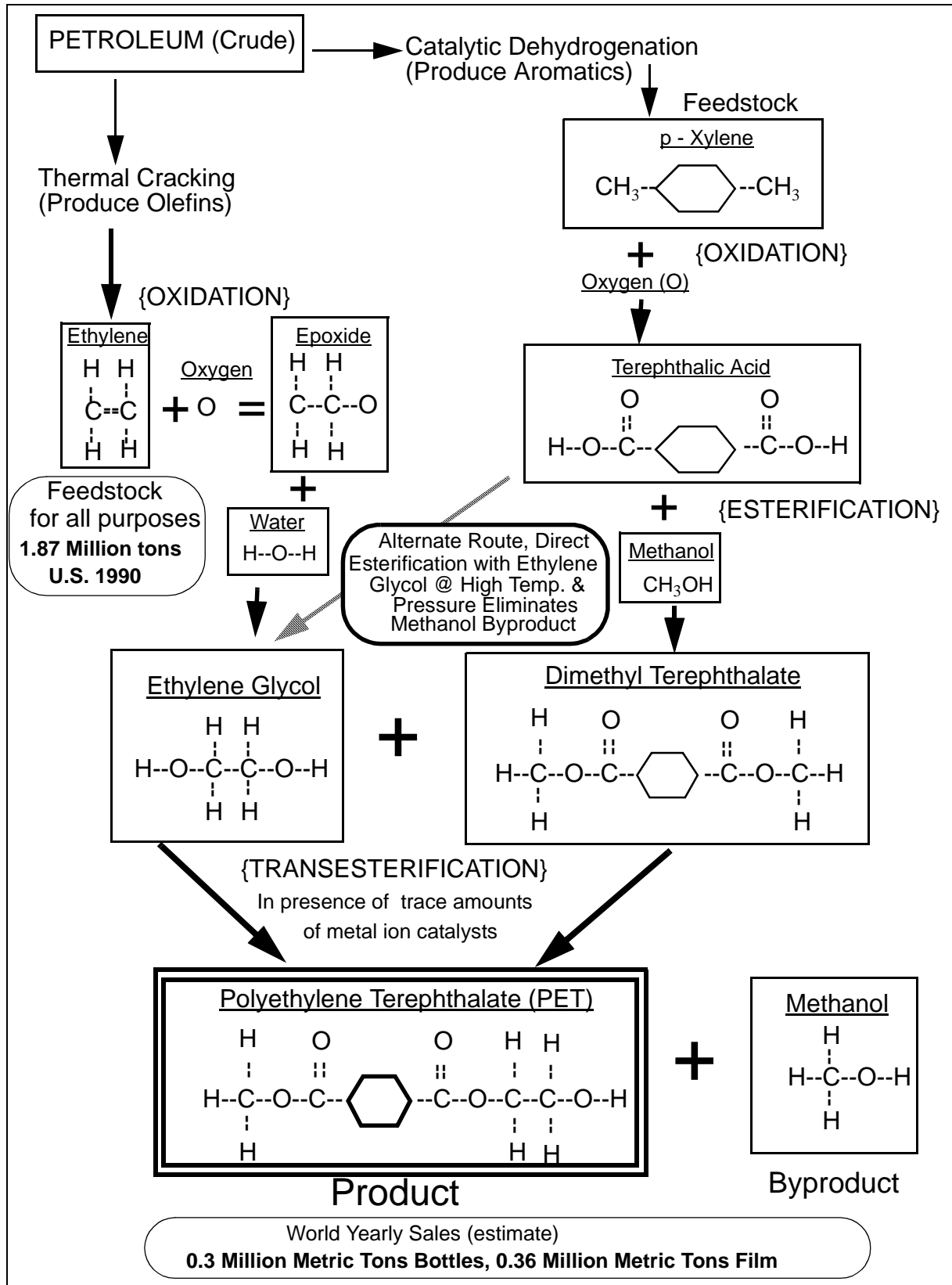


The thousands of plastics that are produced are mainly derived from these feedstocks.

5.9.2 Material Flow in the Production of PET (Polyethylene terephthalate)

PET has been chosen as an example of material flow in the production of plastics because of its importance in the production of beverage containers, films, extrusions, and other products, and the competition that it gives to the production of aluminum cans. Figure 5-16 shows the flowsheet for the production of PET. The chemical formulae are included to describe each step in the production. This flow diagram shown is only one way to get from raw material to bulk PET, and is intended only to give a qualitative idea of the steps that can be involved. However these processes are in general very efficient with little waste. Byproducts (like the methanol shown) are often recycled and reused in some way.

Figure 5-16 Material Flow in the Production of PET



5.10 Material flow in the Production of Paper

5.10-1 Introduction

The primary source of material for the production of paper is fiber from wood obtained from trees. In addition a significant amount of recycled paper is utilized in the production of many grades of paper. A material flow diagram is included in Fig. 5-17 for a mill producing a typical corrugating grade (for cardboard boxes and the like). As in the other material flow diagrams cited in this work, the numbers present are given per ton of product.

Wood is a naturally occurring composite material which consists mainly of a complex array of cellulose cells reinforced by a polymeric substance called lignin and other organic compounds. As indicated in Fig. 5-17, cellulose and hemicellulose make up the largest weight fraction in a given tree with water and lignin close behind. The relative amounts of these components is a function of the type of tree and the extent to which the wood has been dried.

The objective of paper making is to remove the fibrous cellulose from the wood and then press these strands into a sheet of paper.

5.10.2 Energy Requirements for Production of Paper

The energy requirements for a paper mill are quite large, on par with the production of other basic materials and, in the example cited in Fig. 5-17, the energy is provided by combustion of coal and natural gas to produce power to drive the large equipment required to handle the huge daily quantities of materials. In addition a significant amount of the steam generated is utilized in the digester. It can be seen in Fig. 5-17 that approximately 0.4 tons of coal and 2,291,000 cubic feet of natural gas are needed to produce one ton of paper.

5.10.3 Material Flow in Paper Production

Like the other processes presented in this chapter, the production of paper is a very complex, energy intensive process in which significant amount of material flow takes place. The most significant steps involved in the production of this paper (cardboard) are shown in Fig. 5-17 and listed below.

1. Logging trees from woodlots and transporting to the mill.
2. Chipping into an acceptable size for digestion.
3. Screening fines and bark and washing.
4. Dissolve organics (Digesting) in steam heated solution containing Na_2CO_3 to free cellulose from organics.
5. Washing to separate pulp (cellulose) from black liquor.
6. Combusting organics in fluidized bed reactor.
7. Produce paper from washed pulp and recycled paper.

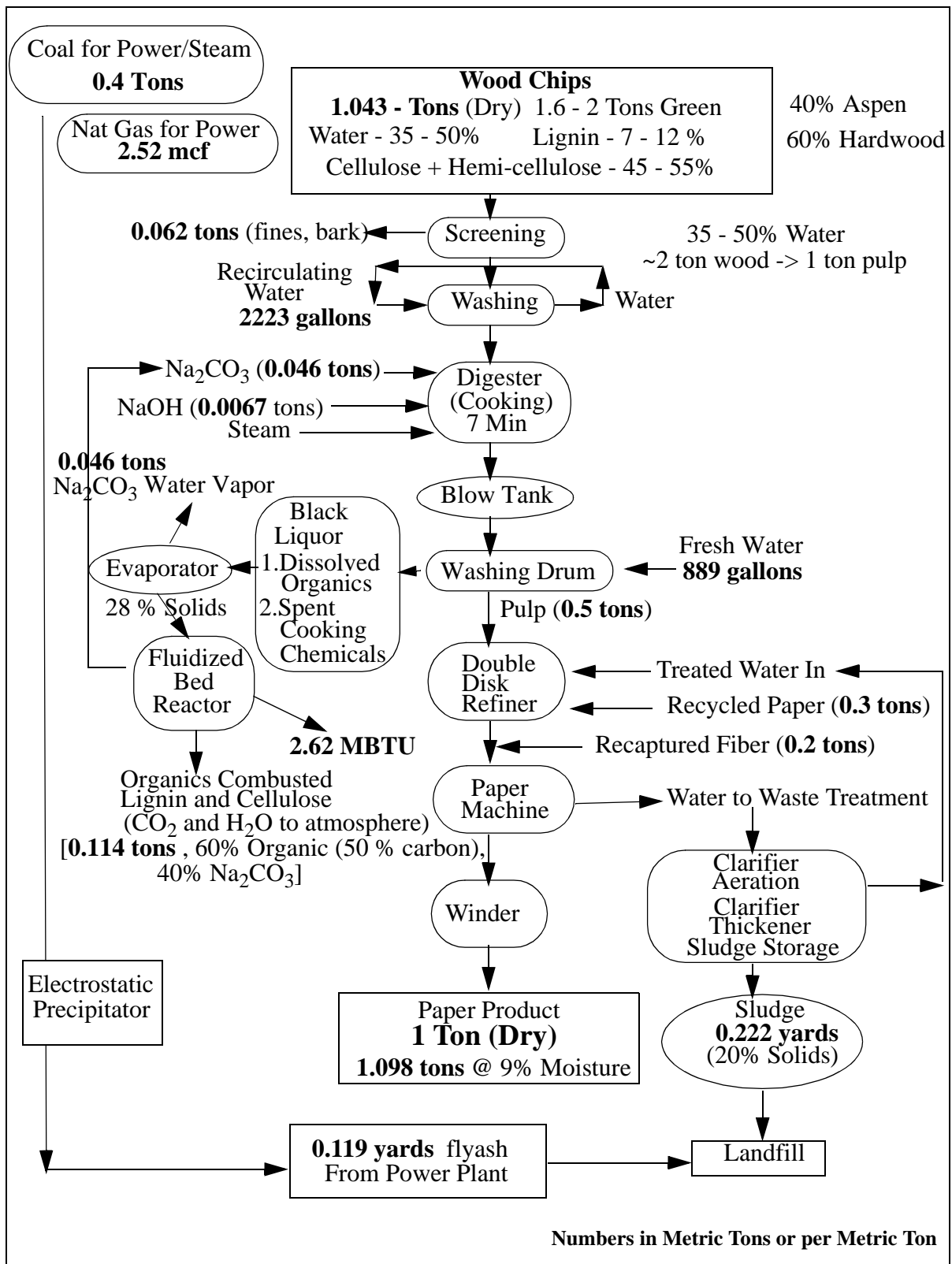


Fig 5- 17 Material Flow in a Typical Corrugating Medium Mill

Figure 5-17 shows that of the original virgin wood, only about half is converted to fiber, the rest of the material being water and other material which ends up in the “black liquor”, the dissolved organics and spent cooking chemicals. Following the action of the digester, the liquor is treated to do the following:

1. Allow water to evaporate.
2. Combust the remaining solids (mostly cellulose) and the dissolved organics in the Fluidized Bed Reactor .
3. Collected the dried (and pelletized) Na_2CO_3 for reuse in the digester.

The pulp fibers are then sent, together with recycled paper and recaptured fiber, to the paper machine for processing into the final product. The recaptured fiber is obtained from many locations in the process.

5.10.4 Environmental Concerns in the Production of Paper

The environmental areas of concern which are evident in this particular process are indicated on Fig. 5-17, and take the following forms.

1. Gaseous Emissions include primarily CO_2 which results from combustion in two places, first from the combustion of coal and natural gas in the power plant, and second from the combustion of the organics (containing about 50% carbon) in the fluidized bed reactor.

2. Liquid emissions in the form of water which is used in the process to wash the fibers of cellulose, removing the organics and fine fibers. This water is treated using aeration, clarification, and eventually returned to the plant. The sludge residue is sent to the landfill as a solid waste.

3. Solid residues from the power plant (flyash, typically amounting to about 10 % of the coal), as well as the sludge mentioned in #2 above.

Problems:

1. Estimate the mass of CO_2 generated per metric ton of paper produced, including output from the fluidized bed and power generation. Compare this to the amount generated in the production of one ton of steel and one ton of cement.
2. Estimate the amount of heat (in BTUs) generated to produce a ton of paper. How does this compare to the amount of heat lost in combustion in the fluidized bed?

5.11 Material and Energy Requirements in the Production of

Copper Oxide

5.11.1 Introduction

All of the previous examples of material flow have involved the use of virgin material in producing a final product. The production of CuO in this section is done to illustrate a flow diagram involving the use of only recycled materials, pure copper-containing materials including most commonly scrap circuit boards and Cu-coated steel. This diagram is shown in Fig. 5-18.

5.11.2 Energy Requirements for CuO Production

The energy requirements for this process include primarily purchased electrical power and natural gas. The power is used to drive the pumps and equipment used to hold and transport solutions, and the natural gas is needed primarily to provide heat energy in the crystallizer, see equation 3* in Fig. 5-18.

5.11.3 Overview of CuO Production

The fundamental process involved here is of a chemical nature, in which Cu is dissolved in solution and then reprecipitated as CuO, which is sold as a solid product. The significant steps involved include:

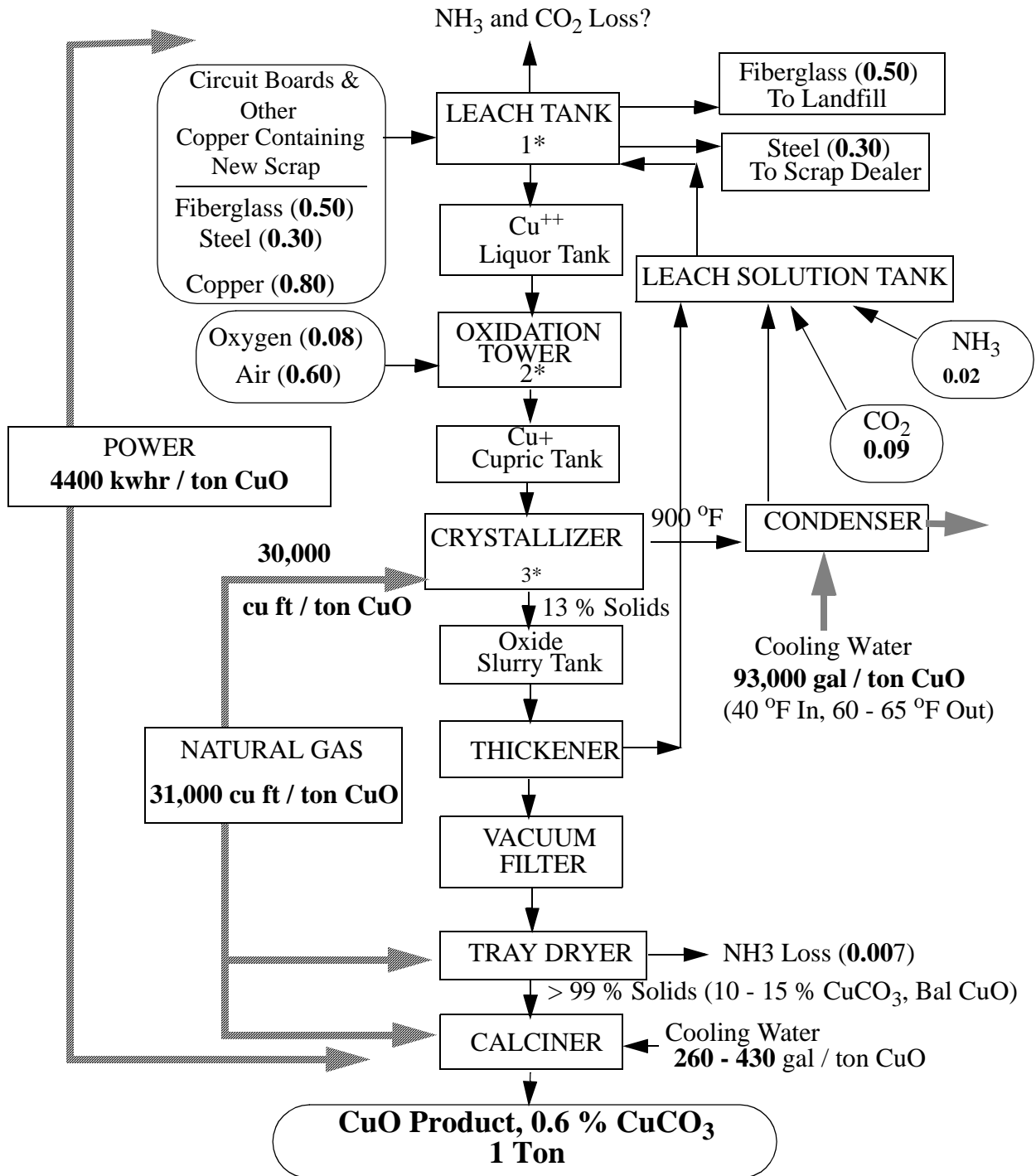
1. Leaching the Cu from the scrap material using a solution containing ammonium ions to produce a cuprous (+1) ion.
2. Oxidation of the cuprous ions to cupric ions (+2).
3. Precipitation of CuO in the presence of CO_3^{-2} .
4. Thickening and filtering the solid to produce a product consisting of a mix of CuO and CuCO_3 .
5. Calcining the CuCO_3 to produce CuO.
6. Bagging and shipping the solid CuO to customers.
7. Marketing the copper-free scrap steel from the leach tanks.

5.11.4 Environmental Concerns in the Production of CuO

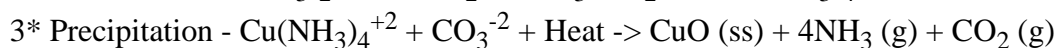
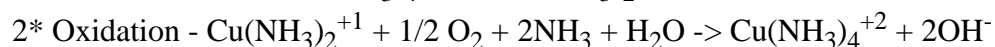
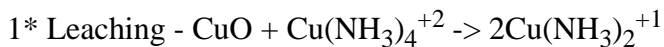
Figure 5-18 illustrates the potential for environmental concern, outputs which mostly result from energy use within the plant. These concerns are listed below:

1. Solids in the form of fiberglass which is landfilled.
2. Gaseous products resulting from combustion of natural gas (mostly CO_2) and the fuel used to produce the power for the plant.
3. Heat which is carried out of the plant in the cooling water.

Figure 5-18 Mass and Energy Flow Diagram for the Production of CuO from Recycled Materials



Numbers in metric tons or per metric ton of product



Problems:

1. Estimate the mass of CO_2 generated per metric ton of CuO produced, including natural gas requirements, CO_2 process requirements and power generation (Assume coal generated power). Compare this to the amount generated in the production of one ton of paper and one ton of cement.
2. Estimate the amount of heat (in BTUs) required to produce a ton of CuO (Include that for power generation and process heat). How does this compare to the amount of heat lost in the condenser?

RECITATION PROBLEMS

The purpose of the following problems is to focus on the generation of the so-called greenhouse gas (CO_2) in the common processes discussed previously in this course, and to compare relative amounts generated in the U.S. and in the world. As is known, CO_2 has been increasing rapidly in the atmosphere and many are concerned that it will lead to global warming (because of the greenhouse effect) if the trend is allowed to continue.

It is estimated that 7 gigatons (7 billion tons) of carbon is emitted into the atmosphere each year as a result of human activity, about 5.3 gigatons from fossil fuel burning and about 1.7 gigatons due to land use (mostly burning of tropical forests).

1. The production of steel as described previously is a material consuming, energy consuming process. In particular, a significant amount of carbon is needed to create steel. Using the mass balance information supplied:
 - (a) Show that the amount of CO_2 added to the atmosphere in the production of one ton of steel as per Fig. 5-5 (1.95 Tons.) is consistent with the chemical compositions of the input materials given in the unit operation data sheets for steel production.
2. Estimate the annual amount of C lost to the atmosphere in creating steel from pig iron for the domestic auto industry. The 1995 Annual Statistical Report of the American Iron and Steel Institute shows that ~14.6 million tons of steel were purchased by the auto industry.
3. Estimate the annual amount of C lost to the atmosphere in the U.S. by:
 - (a) Production of 50 million metric tons of steel from pig iron.
 - (b) Production of 50 million metric tons of steel in electric arc furnaces (EAF). Assume that EAF furnaces charge only scrap and utilize ~650 kwh of coal-fired electricity per ton of steel.

(Pig iron production also consumes electricity, but it is a relatively small amount, 25 kwh per ton of steel.)
 - (c) The power requirements to produce one metric ton of steel from virgin ore are approximately 275 kwh. Again, assuming coal-fired power is used, compute the amount of carbon lost to the atmosphere.

- (d) Compute the total carbon lost in producing steel from virgin ore and compute the “carbon loss savings” on melting scrap vs. recycling.
4. The total world production of steel in 1995 can be roughly divided into 527 million metric tons from pig iron and 225 million metric tons by EAF. Estimate, using your results in Problems 1 and 3, the fraction of the world carbon emission from each method of steelmaking.
 5. Assuming an average automobile gets 27 mpg, burns C_8H_{18} with a specific gravity of 0.7, and travels 15,000 miles per year, determine the carbon lost to the atmosphere (1 gal = 3.785 liter). Estimate the C lost to the atmosphere from all vehicles in the U.S. What percentage of total U.S. C emissions come from motor vehicles? (Assume that the U.S. contributes 25% of the world Carbon to atmosphere/ton = $980.9 - 8 = 972.9$ lb/ short ton steel.