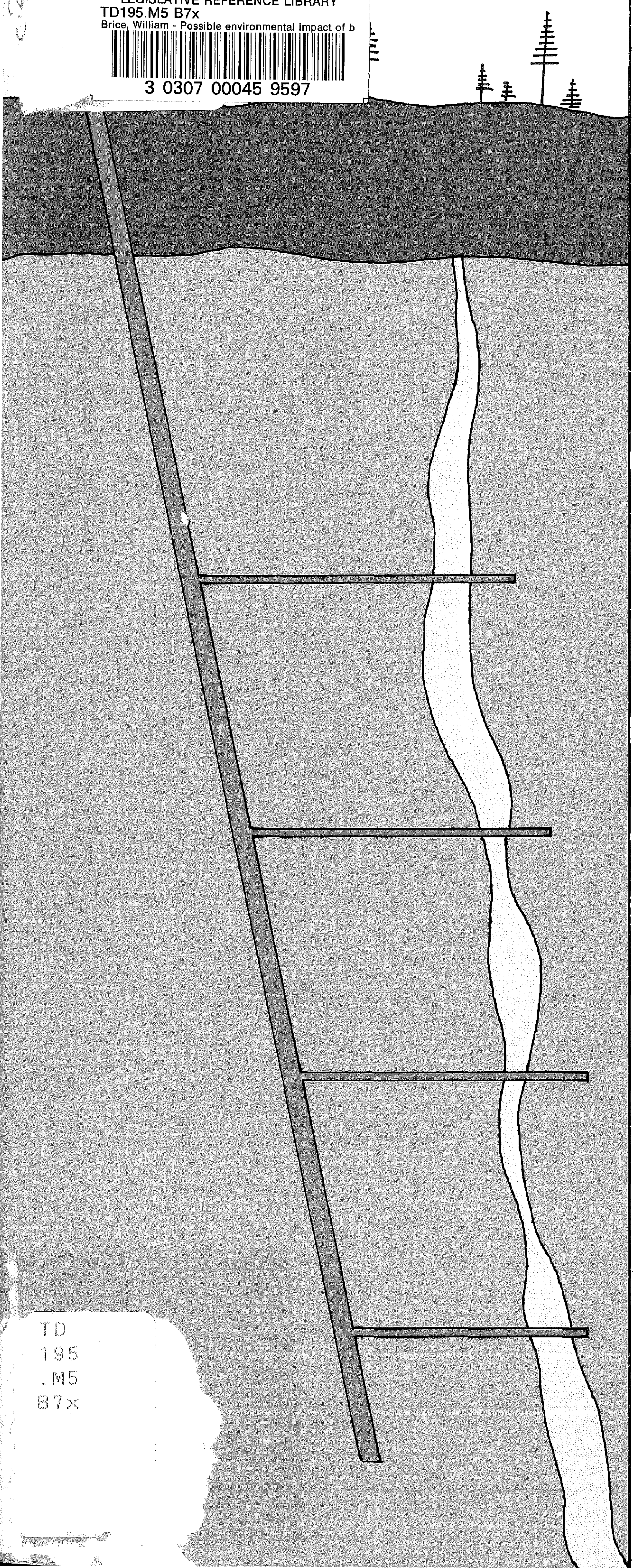

POSSIBLE ENVIRONMENTAL IMPACT OF BASE METAL MINING IN MINNESOTA

MINNESOTA
DEPARTMENT OF NATURAL RESOURCES
DIVISION OF WATERS, SOILS & MINERALS
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POSSIBLE ENVIRONMENTAL IMPACT OF BASE METAL MINING IN MINNESOTA

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SCOPE AND PURPOSE

Minnesota is on the threshold of a new mining industry; that of copper, nickel, and other associated metals. Such an industry could have a substantial impact on the economy and on the natural environment of the state depending upon the mining and processing methods utilized, and the individual circumstances associated with a specific operation.

The purpose of this report is to review and summarize available information on the mining and processing of base metals, such as copper and nickel, in order to provide a guide for planning and evaluating the impact of future mining operations in Minnesota. The report emphasizes advantages, disadvantages, and possible utilization of particular systems, and contains information on probable major environmental factors to be considered in base metal operations. Background information is included in the appendices and a bibliography is provided to assist those wishing to study the subject further.

This report was prepared through the cooperation and assistance of the United States Bureau of Mines, State Land and Forestry Offices, Superior National Forest Office and United States Department of Commerce, National Weather Service Forecast Office.

BASE METAL MINING IN MINNESOTA

The primary potential for base metal mining in Minnesota exists in the Duluth Gabbro Complex, which lies north of Duluth in the "Arrowhead Country", and the Greenstone formations which cover substantial portions of Northern Minnesota. A geologic map showing the generalized location of these two formations is contained in Figure 1.

In view of the concerted effort presently being made in Minnesota and the productivity of similar explored formations just to the north in Canada, base metal mining in Minnesota would appear to be only a matter of time. Based on exploration to date, the United States Bureau of Mines lists the Duluth Gabbro Complex, which contains copper and nickel, as the largest known nickel sulfide resource in the United States[1]. In addition, considerable exploration is being conducted in the Greenstone belts of Minnesota for mineral deposits containing such metals as copper, zinc, lead, gold and silver. This formation is a major source of Canada's mineral wealth, as shown in Figure 2.

In order to study the environmental aspects of future sulfide mining in Minnesota, and in particular the metal extraction phase of such an operation, it is necessary to review the production and recovery methods that might conceivably be used and some of the environmental and production problems that could be associated with these processes.

Markets

Markets, although not directly associated with the environmental aspects of base metal mining, are important because of the by-product sulfur that must be produced, and the fact that the total production costs of the metals will have to include the recovery and sale or storage of a major portion of the contained sulfur. Appendix I contains a brief review of the market outlook for copper, nickel and sulfur. For copper, economists predict a surplus throughout most of the seventies, and early eighties. Prices, however, are not expected to drop below forty-five cents per pound of copper. Expanding nickel markets have caused a nickel shortage throughout most of the sixties. However, additional production capacity coupled with a slowdown in economic growth rates of consuming nations has recently caused an oversupply of nickel on the World market. If all of the planned production capacity goes on line, then the oversupply will probably continue throughout most of the seventies. Because of the many new sources of sulfur, this market appears to be in for a long period of surplus. In Minnesota, the demand for elemental sulfur and sulfuric acid is limited. If little or no local market is found for sulfuric acid, and it appears this will be the case, then the contained sulfur would have to be recovered in a storable form, either as elemental sulfur or gypsum.

Mining Methods

Base metal mining will be substantially different than the present iron ore mining we are familiar with in Northern Minnesota. Although portions of some ore bodies might be amenable to open pit mining, the majority would probably be mined by underground methods due to the characteristics of the formations. Deposits in the Greenstone formation may dictate rather small underground operations, whereas deposits in the Duluth Gabbro formation may support larger scale underground mines and possibly some open pit mines. Any open pit mines would be limited to the areas adjacent to the base of the Gabbro formation where the formation is rather shallow in depth and the stripping ratio small.

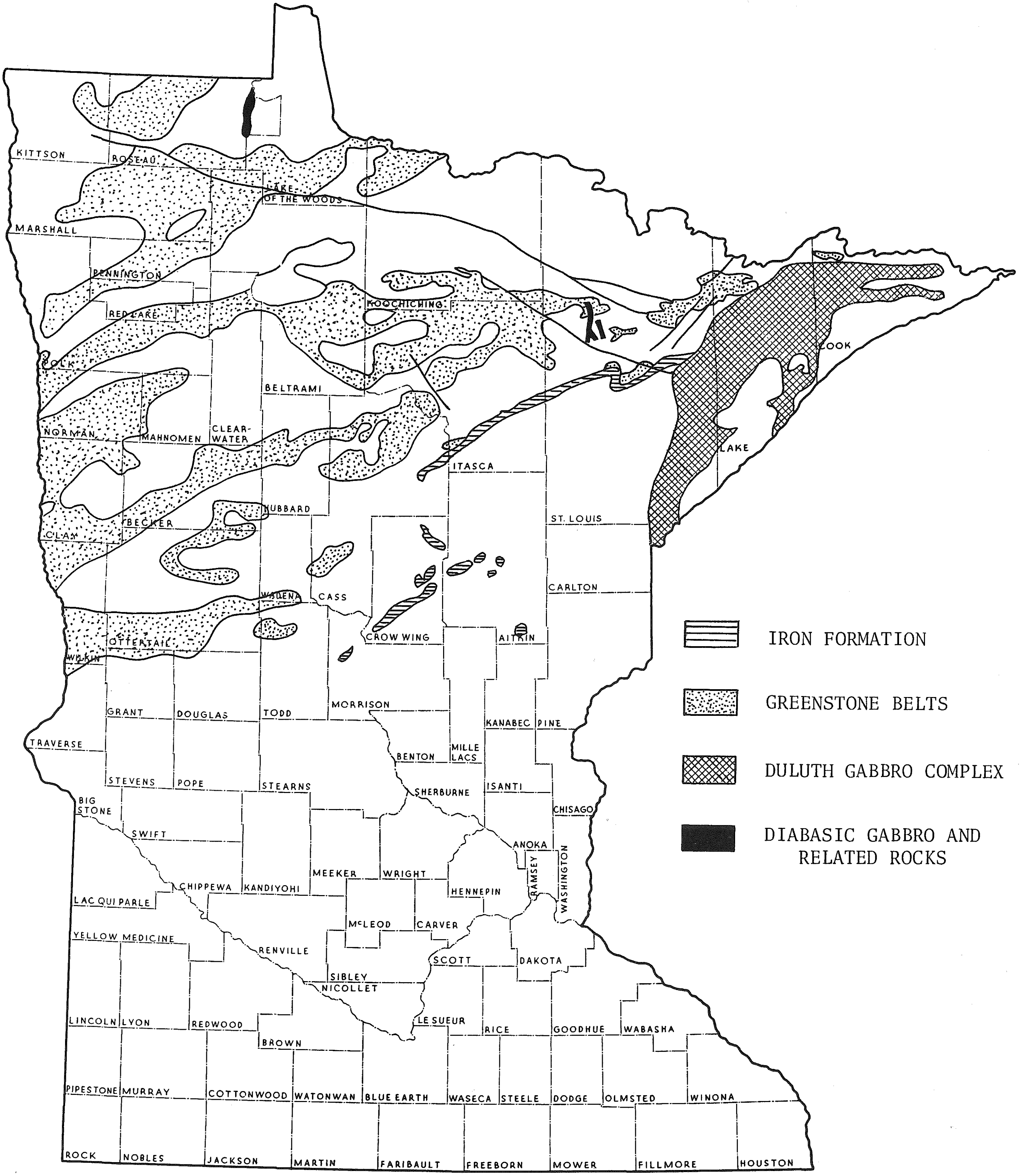


Figure 1 Minnesota Greenstone & Gabbro Formations

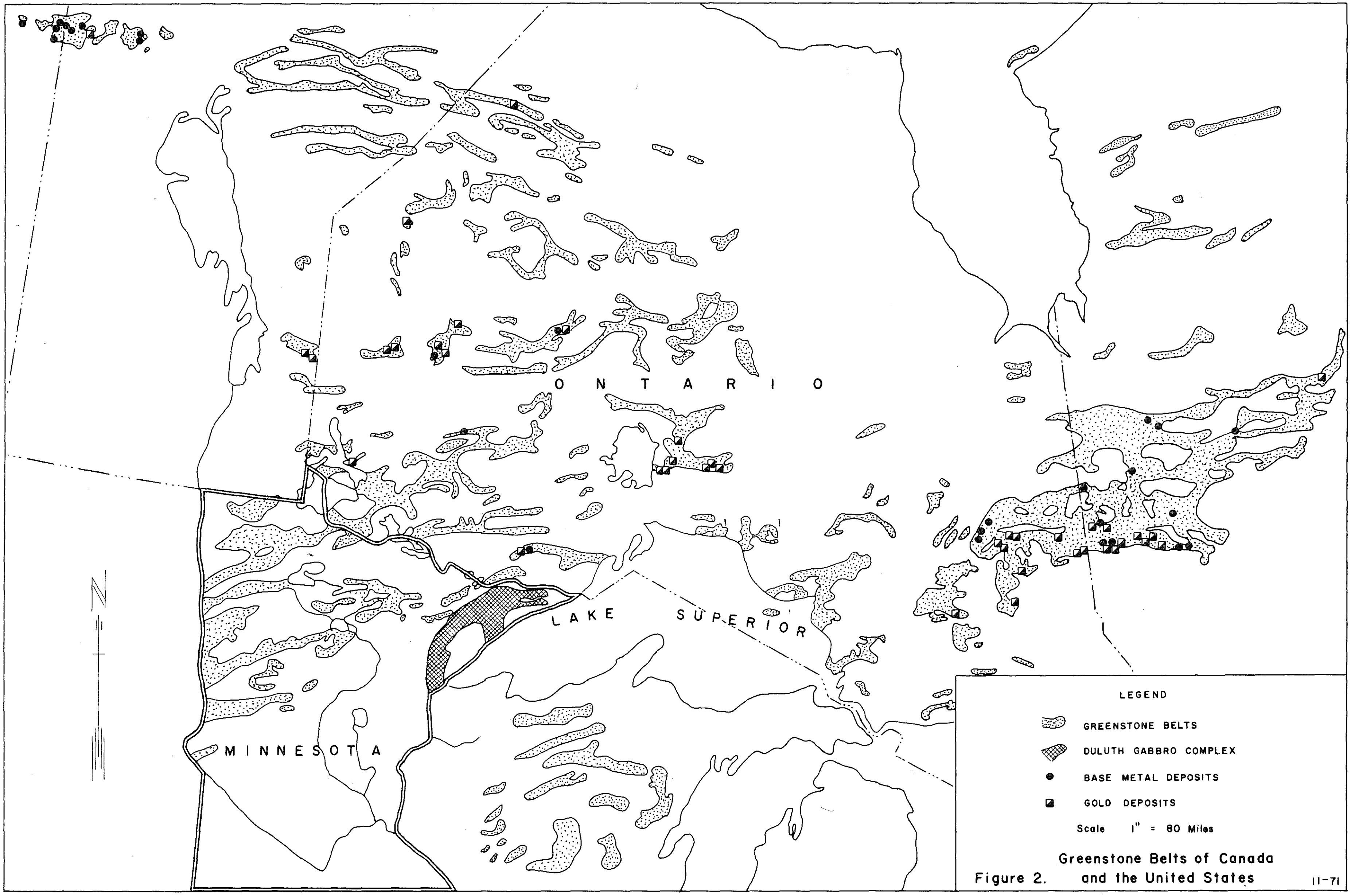


Figure 2. Greenstone Belts of Canada and the United States

Open pit mining along the basal contact of the Duluth Gabbro formation would consist of removal of overburden, drilling and blasting of the rock formations, loading by electric shovel and truck haulage to a primary crusher. Some dust results from trucks on unsurfaced haulage roads, however this can be solved by watering them on a regular basis. The methods to be used for underground mining are open to considerable speculation at this time, but would conceivably be one of the following methods: block caving, room and pillar with high-speed and volume equipment, cut and fill, or sublevel stoping. Depending on the mining method chosen some subsidence might occur. This can be controlled by adjusting the size of the underground openings and relating them to the depth below the surface, or by backfilling techniques[2]. A brief explanation of each of these methods is contained in Appendix II.

Thus far, no deposits of economic value have been announced in the Greenstone belts of Minnesota. If found, they would probably be sulfide type deposits and concentration would be accomplished by flotation.

Water will be required in the grinding and concentrating processes regardless of the methods utilized. Thus, in considering any method, it will be necessary to evaluate water availability and the water pollution potential from any discharges. Assuming that the plant water is recycled, a general rule-of-thumb indicates that about 100 gallons of new make-up water will be required per ton of crude ore processed.

A large portion of the known mineralized area of the Duluth Gabbro formation lies within or adjoins land which is regulated through the actions of Congress known as the "Shipstead-Newton-Nolan Act" and similar action of the State Legislature known as the "Little Shipstead-Newton-Nolan Act" (Minnesota Statutes 1969, Section 110.13). These state and federal acts forbid the artificial alteration of the natural water levels and adjacent shoreland areas in an area of Northeastern Minnesota as shown in Figure 3. The "Little Shipstead-Newton-Nolan Act" was amended by the Laws of 1967, Chapter 556, which modifies the state act to authorize water use for copper-nickel operations in a portion of the area. It appears that similar actions will be necessary under the federal "Shipstead-Newton-Nolan Act" before approval can be secured for water appropriations in the area. Nevertheless, necessary water use and waste water discharge permits must be secured from the Department of Natural Resources and Pollution Control Agency respectively, before commencing any operation. Such permits would be based upon water availability and applicable standards of the state agencies. In addition, any work in beds of public waters requiring a change in the course, current, or cross-section will require a permit from the Department of Natural Resources.

Beneficiation

After the ore has been removed from the ground, whether open pit or underground, it must be beneficiated (See Appendix III). The first step is crushing and grinding. An open pit operation would probably use a gyratory crusher for primary crushing whereas an underground operation might use a jaw crusher for initial crushing. The advantage of the jaw crusher is the smaller space required for installation, which allows it to be installed underground. Secondary crushing would probably be done in cone crushers and the final grinding would probably utilize rod and ball mills. In some cases the rock may be amenable to autogenous grinding, where the ore itself is used as the grinding media. The maximum crushed size might be 1/4 to 3/4 inch, with the final size from the grinding cycle being 200 mesh or finer. The Bureau of Mines conducted tests in 1953 on concentration of metallic sulfides in the Gabbro formation[3,4]. It was found that by crushing and grinding to 200 mesh, a flotation concentrate could be produced which recovered 94% of the copper and 52% of the nickel. Higher nickel recoveries have been obtained by later work using a sulfatization process. Further grinding might also improve recovery somewhat, but some of the nickel occurs as intergrowths in olivine and is probably not recoverable.

Concentrating procedure is more difficult to predict. Two possibilities exist in the Gabbro: a single concentrate could be made and the different metals removed from it selectively, or two concentrates could be made, one containing high nickel and the second containing high copper. This would depend partly on the method chosen for metal extraction. Flotation would certainly be one method used for concentration. It might be augmented by some other method, such as high intensity magnetic separation.

Another environmental consideration to be evaluated in the concentrating process is waste products disposal, particularly tailings. The concentrating process will result in large quantities of tailings; however, the total will be relatively small compared to the expected tailings created from taconite operations. This is primarily due to the magnitude

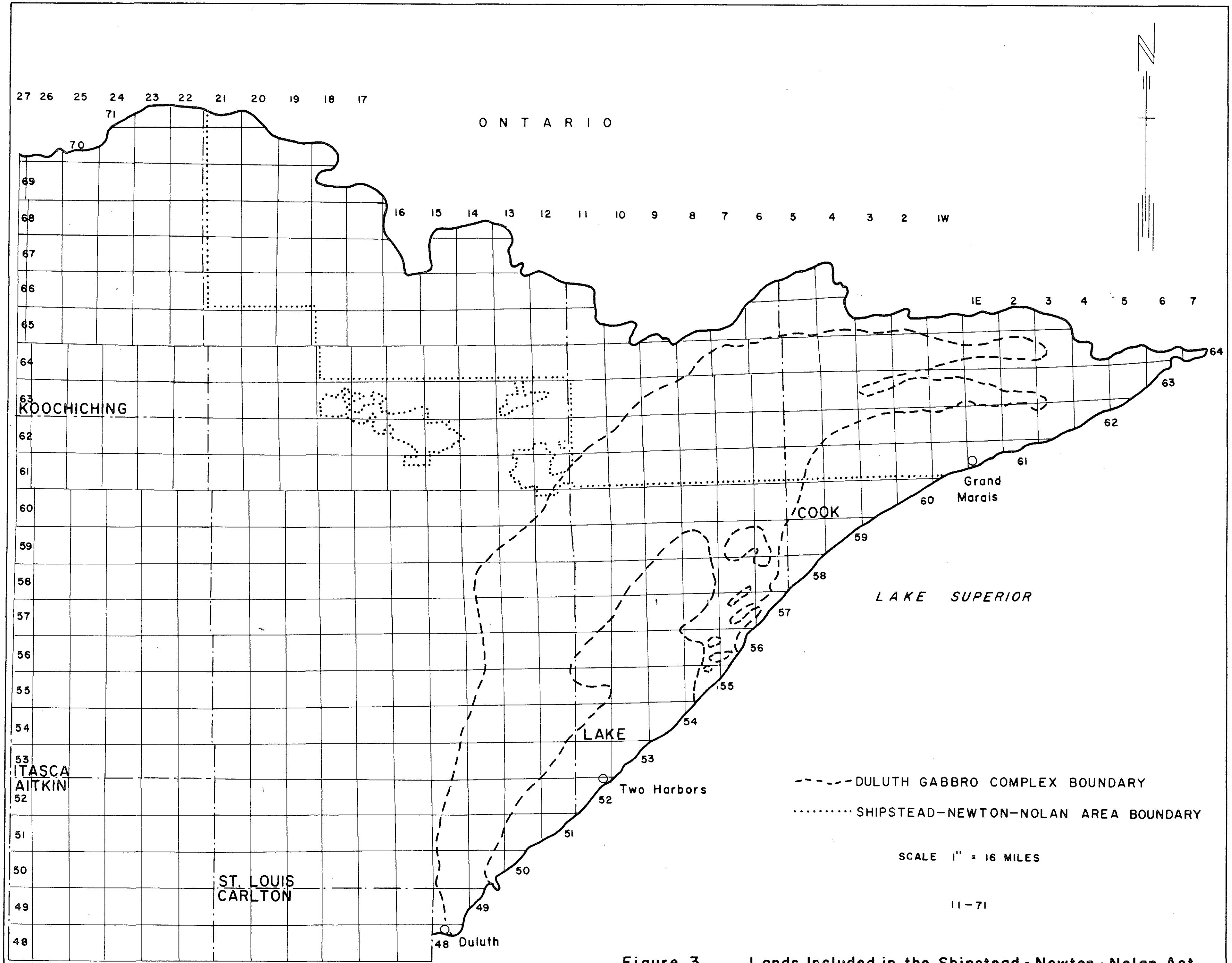


Figure 3. Lands Included in the Shipstead - Newton - Nolan Act

of the operations. Since copper-nickel tailings may contain some soluble materials, care must be taken when selecting a disposal site. It may be necessary to neutralize runoff during the operation. When the operation is completed the areas may require covering and planting to control runoff and prevent erosion. If a cut and fill underground mining method is used, some of the tailings could be deposited underground.

One ton of crude ore containing 1.5% copper will result in approximately 1,900 lbs. of tailings and 100 lbs. of concentrate (Appendix IV lists the general assumptions used). If one hundred million tons of ore were processed in twenty-five years by several mining operations, it would result in 95 million tons of tailings or at 1.5 tons per cubic yard, it would amount to 63.3 million cubic yards. If these were deposited to a depth of 60 feet (20 yards), it would require a composite of basins containing 655 acres or about 16 forties.

Metal Extraction

The third step in the processing of base metals is that of extracting the metal from the concentrate. There are three general groups of metal extraction processes: Pyrometallurgical, Hydrometallurgical, and Vapometallurgical.

Pyrometallurgical processes utilize intense heat to recover the metal. Most of the world's base metals currently are extracted from sulfide ores and concentrates by pyrometallurgical treatment. For many years this method has been the only economical process for treating sulfide ores and concentrates. It includes three sequential operations: roasting, smelting, and converting. These operations are summarized in Appendix V. However, recent concerns with the environmental consequences of such a process has resulted in increased research in improving this process and in developing other processes.

The Sudbury District has often been cited as an example of what environmental effects might result in Minnesota if a Base Metal Industry were to develop in Northern Minnesota. The Sudbury mines and plants were pioneers in the world nickel industry. Processes that were used for concentrating, smelting, and refining evolved from very crude beginnings. Methods used in roasting and smelting caused devastating effects to the surrounding vegetation.

For approximately 40 years before 1932 the ore was roasted in the open on the ground by methods little changed since the middle ages. The following is a description of these early roasting yards. *"After rocky material had been removed by hand sorting on belts and tables, the ore was taken by various means of transports to roast yards where much of the sulfur was removed by its own combustion. This was done by piling heaps of ore upon a foundation of cordwood sufficient to maintain a fire for about sixty hours. The burning cordwood ignited the sulfur, which then continued to burn, sometimes for three or four months or more, until all but ten or eleven percent of the sulfur had been consumed."*[5] To compare the past methods that made Sudbury a name related to desolation with present roasting and smelting technology, would be the same as comparing working conditions prior to the 10-hour day and child labor laws with labor contracts of today.

To extract the metal from concentrate produced from Minnesota ores by pyrometallurgical processes, there are generally two alternatives available to the operator for consideration: either the concentrate must be shipped to an existing facility or a smelter must be constructed in or near Minnesota. There are four existing smelters that might be considered by an operator: two near Sudbury, Ontario, one at Riddle, Oregon, and one at White Pine, Michigan.

1. Falconbridge Nickel Mines, Ltd.
   Falconbridge, Ontario, Canada

2. International Nickel Co. of Canada, Ltd.
   Copper Cliff and Coniston, Ontario, Canada

3. Hanna Mining Company
   Riddle, Oregon

4. White Pine Copper Company
   White Pine, Michigan

Probably all of the above facilities would have to be modified in order to handle the metallurgy of Minnesota concentrates and enlarged to handle the additional material. Likewise, such an arrangement would require intercompany agreements for processing the ores.

The Riddle, Oregon facility only smelts nickel concentrates and the White Pine facility only smelts copper.

If a single concentrate were made from the Minnesota ore, major changes would have to be made in either facility. If two concentrates were made, changes would still be necessary, but probably not as many. In this second case, the nickel concentrates could be sent to Oregon and the copper concentrates to White Pine. A major consideration in a plan like this would be the large transportation costs.

Falconbridge has shown no interest in Minnesota mineral properties to date. Transportation costs to its plant would be high, and modifications to handle the metallurgy would be necessary.

The International Nickel Company (INCO) owns the most likely existing facilities chiefly because INCO holds leases in Minnesota and has already conducted a preliminary evaluation of the economics of an ore body in the Gabbro formation. Most of the problems, such as difficult metallurgy, high transportation costs, and limited capacity still exist. In addition, other companies interested in Minnesota copper-nickel ore might not have access to the INCO smelters.

Therefore, it is probably safe to conclude that if mining is done within the Duluth Gabbro Complex, it will be necessary to build some type of metal extraction facility within the state. If ore bodies are found in the Greenstone belts, they would probably be small, relatively high grade deposits. The concentrates from these could either be sent to a custom smelter on a contractual basis or a Minnesota facility could be built to accommodate several operations.

Hydrometallurgical processes are operations in which aqueous solutions play a predominant role to recover the metal. This process, commonly called leaching, is used to treat oxide ores; and some sulfide and mixed ores of marginal grade (Appendix VI). However, as yet, no process of this type is available to treat copper-nickel sulfides economically

Vapometallurgical processes employ various gases as the primary performers. There are apparently no processes of this type currently being utilized for metal extraction. International Nickel refines nickel using a vapometallurgical process involving carbon monoxide at atmospheric pressure. The feed material is a granular nickel oxide which has been roasted[6].

If an extraction system to treat sulfide ores were to be built today, the only proven process available would be a pyrometallurgical type. Some possible alternate extraction processes which are being studied will be discussed later.

The amount of water to be appropriated and the type of waste products that will be produced during extraction depends on whether the method chosen is hydrometallurgical or pyrometallurgical. Estimates of these are shown in Table 1.

Table 1 Estimate of Water Requirements and Waste Products

Water Appropriation

1. Pyrometallurgical Extraction
   25–50 gallons of new make-up water are required per ton of crude material processed.
2. Hydrometallurgical Processes
   100 gallons of new make-up water are required per ton of crude material processed.

Waste Products

1. Pyrometallurgical Extraction
   Slag is produced at the rate of approximately 1500 lbs. per ton of concentrate.
2. Hydrometallurgical Extraction
   Tailings, possibly containing soluble salts, are produced at a rate of approximately 1500 lbs. per ton of concentrate.

Refining

The final step in processing is refining. Refining is reviewed in Appendix VII. If the extraction method is hydrometallurgical, the probable final product would be refined metal. However, if the method is pyrometallurgical, then either the metal would be refined elsewhere by an existing refinery or possibly in a new refinery in Minnesota. Refining is usually done in a closed system by electrolysis. The primary environmental problem would be the disposal of small quantities of slimes.

AIR POLLUTION PROBLEMS ASSOCIATED WITH PYROMETALLURGICAL EXTRACTION

In the recent drive for cleaner air, the nation's smelters have come under strong attack. Two air pollution problems associated with the traditional pyrometallurgical approach to base metal extraction are (1) excessive dust, and (2) sulfur oxide emissions.

Dust recovery technology is sufficiently advanced so that suspended particulants can be recovered. Appendix VIII describes several of the available processes. The Minnesota Pollution Control Agency Standards for sulfur dioxide and particulant control are published in Air Pollution Control Rules, Regulations, and Air Quality Standards, Chapters 1, 3 and 5. These standards would have to be met by any smelter built in Minnesota.

Before further consideration of federal and state emission control proposals, it is important to review the environmental effects of sulfur dioxide in the atmosphere (See Appendix IX). It appears that sulfur dioxide by itself and in small quantities ($<$ 0.1 ppm) may not be particularly harmful. When it is allowed to interact with other pollutants such as particulants and ozone, or when weather conditions cause the sulfur oxides to concentrate, severe damage can result.

In order to help predict periods of high air pollution potential or air stagnation, the National Air Pollution Weather Forecast Program was created. Appendix X outlines the basic meteorological parameters used to evaluate air pollution potential and their use.

If a company considered building a smelter in Minnesota, a study of meteorological parameters including wind conditions would be necessary. In order to facilitate such a study, the Department of Natural Resources has collected data on surface winds from 21 stations in Northeastern Minnesota (See summary Figure 4). The data was collected during the seven-month fire seasons in 1969 and/or 1970. Upper wind conditions were also obtained for Northwestern Minnesota. The information and data collected are listed in Appendix XI as source material for further study either on a large or small scale basis.

In the smelter, SO_2 is derived from several sources. *"One-third to one-half of these SO_2 emissions are usually generated at reverberatory furnaces, and one-half to two-thirds are generated at converters, depending on the smelter. Alternatively, at some smelters, roasters are used to treat concentrates before they are charged into the reverberatory furnaces, producing a roaster off gas of sufficient SO_2 concentration for sulphuric acid manufacture while at the same time limiting SO_2 discharged at the reverberatory furnace. And finally, if there is an acid plant at the smelter, there are also acid plant tail gases containing SO_2 for the producer to contend with."*[7]

When the reverberatory furnace is treating unroasted concentrates, a steady flow of very low concentration SO_2 is produced. The concentration is often less than 1% of the total gas volume. Converters can produce strong gases running in excess of 6% SO_2. However, because conversion is a batch process, gases produced vary in concentration. The roaster, when used, produces fairly strong concentrations of SO_2 gases and in constant volumes.

There are basically three procedures that have been used to eliminate or decrease the effects of SO_2 emissions. Tall smokestacks are used to help speed the dispersion of gases emitted. Appendix XII briefly describes the theory and use of tall stacks. Second, when a market is available, some sulfur is removed from the stack gases as either sulfuric acid, or elemental sulfur. Appendix XIII lists several of the removal systems being developed. Lastly, some companies curtail production when concentrations of sulfur oxides in the atmosphere are too high or expected to concentrate (Appendix XIV).

When considering sulfur oxides, three types of emission control proposals are currently being considered at the state and federal level. *"First, ambient air standards based on federal recommendations have been universally adopted in the copper producing states. Second, a federal recommendation that the copper smelters be required to control 90% of the sulfur in their smelter feed has become law in Arizona and Montana . . .; has been adopted by the Puget Sound Air Pollution Control Agency; and is under consideration in other copper smelting states. And third, a proposal for a tax on all sulfur emissions is now being considered at the federal level."*[7]

"Most copper industry leaders agree that current federal ambient air standards can be met without major disruptions to copper production. However, they feel that compliance with the 90% standard is still a very "iffy" proposition technologically, and in the case of some smelters, it may mean financial disaster. And they believe that the imposition of a sulfur emissions tax on top of the expense of meeting the ambient air and emissions standards would be ruinous for the entire U.S. copper industry."[7]

Sulfur in the atmosphere comes from a variety of sources. About two-thirds are due to natural processes, and man contributes about one-third of the total sulfur. Since sulfur gases are not stable over long periods of time in the atmosphere, there is no build-up on a world basis. The problems which the copper producers face is that their smelters cause high concentrations of SO_2 in the specific areas in which they operate.

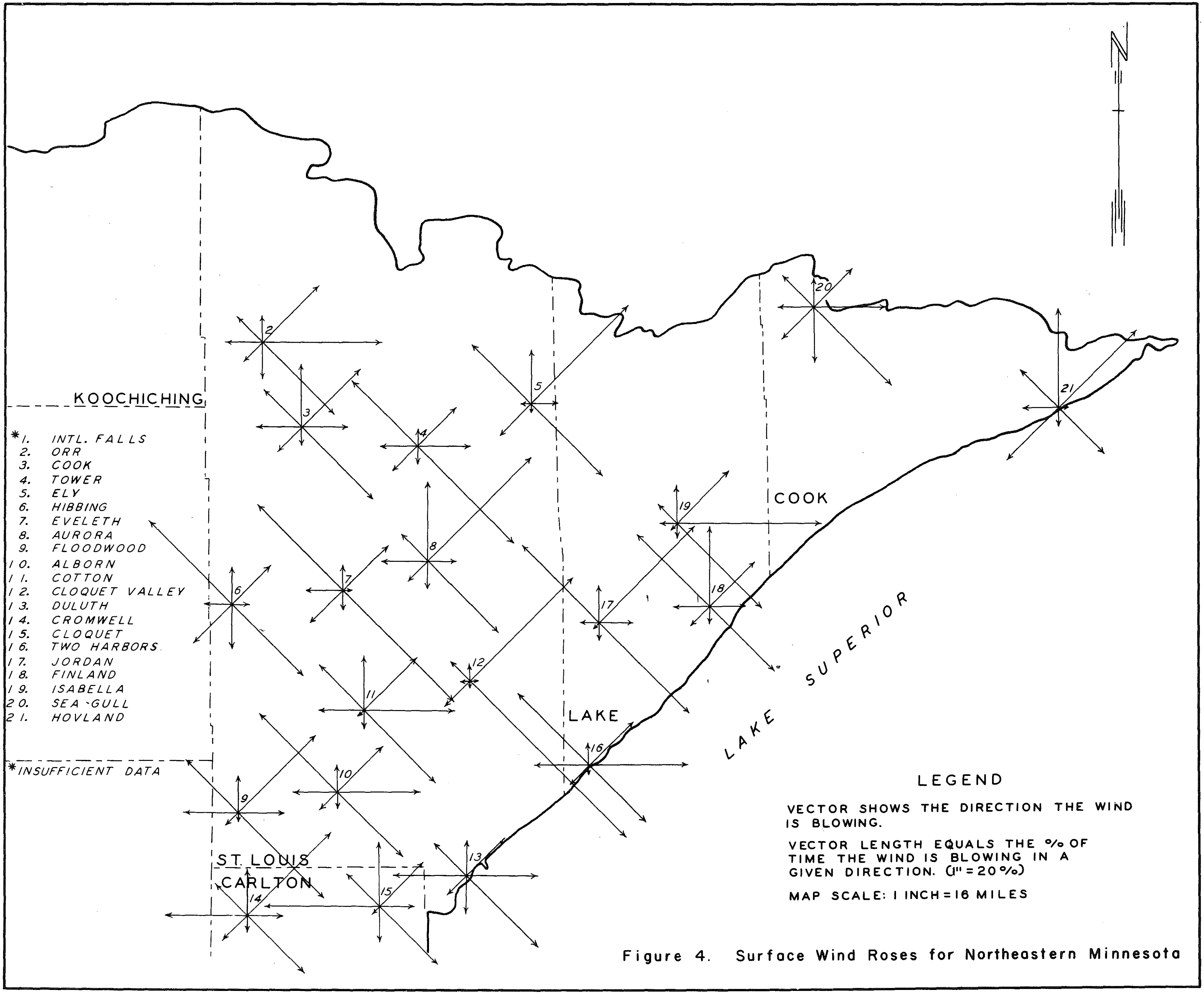


Figure 4. Surface Wind Roses for Northeastern Minnesota

ALTERNATIVE EXTRACTION METHODS

High pollution standards, economics of sulfur recovery, and recently the threat of a tax on sulfur emissions have forced industry and government agencies to spend large sums of money on two general areas of research. The first, which was discussed previously, is the control of sulfur emissions from existing smelters (partial sulfur recovery, tall stacks and curtailed production) and the second, which will be discussed here, is to replace some or all of the traditional smelter by an extraction process whose effluents can be successfully controlled. These replacement systems will be discussed briefly with emphasis on whether the new system will meet air pollution standards, the relative environmental costs, and what reserves would be necessary for such an extraction facility to be built in Minnesota.

There are basically three groups of alternative extraction processes proposed to replace the traditional smelter: pyrometallurgical extraction (traditional smelting is a member of this group), hydrometallurgical extraction (oxide leaching is a member of this group), and combination systems which combine both pyrometallurgy and hydrometallurgy.

Pyrometallurgical Methods

At least four systems in the pyrometallurgical group are being considered to replace conventional smelting: continuous smelting, flash smelting, blast furnace smelting, and electric furnace smelting. Appendix XV describes each system and its relative merits. All of the above systems have been operated successfully on a commercial scale with the exception of the continuous smelter. Two types of continuous smelting have been tested in pilot plants, and commercial prototypes of the Noranda and WORCRA Continuous Smelters are currently under construction. The continuous smelter combines all three traditional steps into one process. This will produce high concentration SO_2 gases which, because of the concentration, should be recoverable. The flash smelter combines roasting and reverberatory steps but leaves the converting step essentially the same as in traditional smelting. Magma Copper Companv apparently feels that the SO_2 from the converters can be successfully treated and has, therefore, announced plans to replace its reverberatory furnaces with flash furnaces. The blast furnace also combines roasting and reverberatory steps, but, only lump ore or sintered concentrate can be treated successfully due to extreme dust problems. The electric arc furnace is desirable when low cost electricity is available, but the converter off-gases are still a problem.

Hydrometallurgical Methods

Two types of hydrometallurgical systems are being considered in the pilot plant development stage to treat copper sulfide ores and concentrates. These systems are reviewed in Appendix XVI. If successful, these processes could completely eliminate air pollution control problems. However, it is possible that they could produce a completely new group of water pollution problems. Appendix XVII considers two types of problems: loss of leaching solution, and disposal of leaching residuals.

Combination Methods

The last system combines pyrometallurgy with hydrometallurgy. The sulfide concentrates are roasted and the metal is removed by leaching. Appendix XVIII discusses work done by Sherritt Gordon and the Bureau of Mines.

Comparison of Extraction Methods for Use in Minnesota

It is helpful at this point to take several of the above systems and compare them in a hypothetical Minnesota facility. In the July, 1971 issue of the Engineering and Mining Journal, a table was printed which summarized copper smelting capacity in the United States. This appears as Appendix XIX and is useful for comparison purposes.

For our evaluation and comparison, traditional smelting, flash smelting, continuous smelting, combination smelting, and sulfide leaching were chosen. The blast furnace and electric arc furnace are not considered herein because air pollution problems associated with the converter are similar to those of the flash furnace. Air pollution problems of the two known continuous smelting methods (Noranda and WORCRA) appear to be similar and accordingly, the Noranda process is used as a basis for continuous smelting in a hypothetical Minnesota plant. Likewise, in considering sulfide leaching, possible water pollution problems are common to both the Anatread and Duval processes.

For each system, a minimum plant capacity was chosen based on the process step with the minimum capacity. From this minimum plant capacity, minimum ore reserves were calculated on a twenty-five year supply basis with ore containing 1.0 and 1.5 percent copper (Table 2). Appendix XX shows these calculations. Since copper is the predominate metal contained in the ore of the Duluth Gabbro formation, the nickel was not considered in the extraction comparison.

Finally, an attempt was made to compare possible environmental costs for each system. It was assumed that dust recovery costs would be negligible compared to sulfur recovery costs, and that, due to Minnesota's limited sulfuric acid market, elemental sulfur would have to be recovered. The recovery system chosen was the citrate process chiefly because pilot plant studies show it to be one of the cheaper methods for recovering elemental sulfur. The Bureau of Mines study showed a cost of $35 per ton of sulfur when treating 2% gases. This cost according to the Bureau would include amortization and operating costs[8]. The 2% SO_2 gases would probably correspond to those produced in the reverberatory furnace and the converter. When stronger gases were produced, a cost of $28 per ton of sulfur was assumed. These gases would probably correspond to those produced in the roaster, flash furnace, and continuous smelter. Finally, it was assumed that the elemental sulfur recovered could be sold for $15 per ton. Appendix XXI contains these calculations. Table 2 summarizes the results of reserve estimates and environmental costs.

The last step in reviewing metal extraction methods is to consider what some of the major companies are doing to reduce or solve their sulfur pollution problems. A literature survey was made and Appendix XXII summarizes by company some of the steps which are being taken.

APPENDIX I: FUTURE MARKETS FOR COPPER-NICKEL RESOURCES

The decision to mine an ore body depends on a number of economic factors: how much metal is available, at what cost can it be produced, and for what price can it be sold. With this in mind, a review of future copper, nickel, and sulfur markets was made.

Copper

The demand for copper depends primarily on two industries: electrical and construction. Other users include: transportation industry, appliance manufacturers, and large machinery producers.

Copper prices have a notorious reputation for fluctuating. Recent predictions by Jay Parkinson forecast a "theoretical surplus" of 500 million pounds in 1973. These surpluses are to peak out at 1.7 billion pounds in 1975, and move back to equilibrium in the late 70's and early 80's. However, it appears that the estimated surplus for 1971 may have been reached in 1970, thus moving up the entire estimate one year.

Because of the environmental demands on the industry, copper prices may soon be controlled by smelting capacity rather than available concentrates. Already there are quantities of concentrates waiting to be smelted while the price of refined metal is holding fairly strong.

In the past two years, the price of copper has dropped from a high of 60 cents per pound to a low of 50 cents per pound and then recently rebounded to 52.57 cents per pound on the U.S. market and 51.35 cents per pound on the European market (May 1972). Many economists predict that copper prices will continue to decrease gradually but will not go below 50 cents per pound on the U.S. market. This they feel is due to production costs, particularly environmental costs, which have increased rapidly in the past few years. It has been estimated that 45 cents per pound is about the absolute minimum price that could maintain acceptable profitability for the industry.

There are many copper producers in the United States, the largest being in the Western States. Arizona is presently the largest copper producing state followed by Utah, New Mexico, Nevada, and Montana.

Nickel

The largest use of nickel is in the manufacturing of stainless steel. Other important uses include: alloys, nickel plating, and castings.

Throughout most of the sixties, markets expanded rapidly. However, additional production capacity, coupled with a slowdown in economic growth rates of consuming

TABLE 2: SUMMARY OF POSSIBLE EXTRACTION METHODS AND ESTIMATE OF ENVIRONMENTAL COSTS

Extraction Method	Traditional Smelting	Flash Smelting	Continuous Smelting	Combination System	Sulfide Leaching
Extent of Development 5-72	Commercial	Commercial	Commercial Under Construction	Bench Model	Pilot Plant
Process Steps	Roasting Reverberatory Converter	Flash Furnace Converter	Continuous Furnace	Roaster Leaching	Leaching
Minimum Size Determinant	Reverberatory Furnace	Flash Furnace	Continuous Furnace	Roaster	Leaching Tanks
Assumed Minimum Plant Capacity	225 tons/day Blister Cu	230 tons/day Blister Cu	150 tons/day Blister Cu	100 tons/day Pure Cu	50 tons/day Pure Cu
Ore Reserves Necessary for a 25-Year Supply (ton)					
1.5% Cu	155,000,000	159,000,000	103,000,000	71,000,000	36,000,000
1.0% Cu	233,000,000	237,000,000	153,000,000	106,000,000	53,000,000
Possible Pollution Control Problems	SO_2, Dust	SO_2, Dust	SO_2, Dust	SO_2, Dust Soluble Salts	Soluble Salts
Estimate of Sulfur Recovery Costs Using the Citrate Process for a 25-Year Ore Supply Total (Capital + Operating)	$245,000,000	$247,000,000	$160,000,000	$55,000,000 in Roasting Steps Leaching Unknown	Unknown
Cost Per Lb. of Cu Recovered	.84¢/lb. of Blister Cu	.85¢/lb. of Blister Cu	.86¢/lb. of Blister Cu	.17¢/lb. of Pure Cu in the Roaster	Unknown
Can it Meet Pollution Standards	No	Possible Problems in Converter	Probably	Unknown	Unknown

nations, and large cutbacks in the aircraft and space industries, has since caused an oversupply of nickel in the world market. If all of the planned production capacity goes on line, then the oversupply will probably continue throughout most of the seventies. The present published price for nickel is $1.33 per pound on the U.S. market. However, it is expected to drop somewhat unless production is controlled.

There is currently only one nickel deposit being mined in the United States. This deposit owned by Hanna Nickel Smelting Company at Riddle, Oregon produced approximately 26 million pounds in 1968. The Bureau of Mines[1] lists Minnesota as having one of the largest potential nickel sulfide resources in the United States.

Sulfur

Most of the sulfur used in the United States, is in the form of sulfuric acid. Of the total demand for sulfur, somewhat over half is used in the fertilizer industry. Lesser amounts are used in leaching processes, petroleum refining and in the manufacture of titanium dioxide, cellophane, rayon, iron and steel and hydrofluoric acid.

Because of the high percentage of sulfur used in the fertilizer industry, growth rates in sulfur consumption are linked to growth rates in fertilizer production. Fertilizer production presently is growing only slightly if at all.

With the many new sources of sulfur anticipated from required future recovery systems, and with the high sulfur content of Canadian natural gases, the sulfur market appears to be in for a long period of surplus. Therefore, unless pricing and production restraints are initiated, the price of sulfur should continue to drop.

The sale of sulfuric acid is not only limited by the demand, but also by the distance to market. Sulfuric acid is expensive to ship and store, so unless a nearby market is available, it would have to be produced and stored as elemental sulfur.

In Minnesota, the demand for sulfur and sulfuric acid is quite limited. However, exploration has shown substantial reserves of titaniferous magnetite, and more recently during copper-nickel exploration, titanium has been found north of Duluth in the Duluth Gabbro Complex. If these deposits were to be mined, sulfuric acid would be required for processing.

APPENDIX II: UNDERGROUND MINING METHODS

Block Caving

This is a method of mining ore in successive layers from the top down. Each block is undercut over the greater portion of its bottom area. The supporting pillars are blasted out and the overlying block caves causing the rock to crumble.

Room and Pillar With High-Speed and Volume Equipment

In this method, the ore is mined in rooms separated by narrow ribs or pillars. The ore in the pillars is removed by subsequent working, in which the roof is caved in successive blocks.

Cut and Fill

Also called overhand stoping, this is a method where stopes are excavated in a series of horizontal slices either sequentially or simultaneously from the bottom of a block to its top. The stopes are usually refilled with waste material as the mining progresses.

Sublevel Stoping

This method's characteristic feature is the use of sublevels. The sublevels are worked simultaneously, the lowest on a given block being farthest advanced and the sublevels above following one another at short intervals.

APPENDIX III: BENEFICIATION OF SULFIDE ORES

Copper and nickel beneficiation consists of a series of mechanical steps that concentrate the contained metals by separating them from the unwanted gangue minerals. Most ores being mined today are low grade disseminated deposits in which metallic sulfides occur as very small grains or as intergrowths with other minerals. To extract the desired mineral grains, they first must be released from the surrounding gangue minerals by crushing and grinding, after which the sulfides are separated by various concentration processes. The gangue minerals are disposed of as a thin slurry of powdered rock in water called tailings, and the concentrate is dewatered in preparation for metal extraction.

Crushing and Grinding

The usual crushing procedure is as follows: The ore is crushed at the mine in jaw or gyratory crushers to a size suitable for transportation and mill handling. At the mill, the ore is crushed further by gyratory type cone crushers, followed by roll crushers. The final stage is achieved by grinding. One of two methods can be used: (1) sequential grinding in rod and ball mills, or (2) autogeneous grinding. If at any time in the crushing or grinding steps the ore is not fine enough, the coarse portion is returned to a previous step. Screens are used to size the ore in the coarse stages, but are not effective in separating the material after fine grinding. Classifiers are used for separating the fine material. The ground ore is sized by the speed with which it settles through a liquid medium. There are two types of classifier commonly in use, the hydraulic cyclone and the mechanical classifier.

Concentrating

Following crushing and grinding, the ore is ready for concentration. In copper and nickel metallurgy, these operations are normally based on the surface characteristics or the magnetic susceptibility of the particles. The most widely used method is froth flotation.

The operating principle in flotation is the lifting action of soapy air bubbles rising through a column of pulp. Depending on the reagents added to the pulp, certain mineral particles adhere to the bubbles, and the remaining particles settle by gravity. The minerals that the bubbles "float" to the surface are skimmed off in a froth, and the minerals that sink are rejected as underflow. The process takes place progressively through a bank of cells to provide adequate opportunity for the floatable particles to contact bubbles. Both copper and nickel can be separated from the silicate gangue by this process.

A second method used for concentrating nickel sulfides is magnetic separation. This method is based on the fact that minerals differ in the degree to which they are attracted by a magnetic field.

Dewatering

Concentrates come from the flotation machines as a dilute slurry. Some or all of this water must be removed before further treatment. Dewatering is usually done in two stages. Thickening settles the solids by gravity so that the overlying liquid can be decanted. Filtration then removes most of the remaining water. A thickener works on the same principle as a settling basin; it is a circular tank with a central feed well, a peripheral overflow rim, and a bottom-raking mechanism to remove the sludge concentrate. In the second step, filtration, solids are separated from fluid by causing the fluid to pass through a fine septum (fabric) that will not allow the solids to pass through.

APPENDIX IV: ASSUMPTIONS USED IN THE VARIOUS CALCULATIONS

Because of the early stage of exploration in Minnesota, it is impossible to make any calculations without first making several assumptions. For reserve estimates, ore grades were assumed to be 1.5% Cu and 1.0% Cu. Since nickel is the secondary metal, it was assumed to be negligible. In actuality, the value of the nickel which could be recovered would be added into the total value of the ore. It was also assumed that if a smelter were built in Minnesota, twenty-five years would be necessary for its amortization. A minimum annual metal production was assumed for each extraction method by reviewing the literature.

In order to calculate the necessary reserves of crude ore from a yearly metal production, the following assumptions had to be made regarding concentrating and extraction.

1. It was assumed that a copper concentrate containing 25% Cu would be produced. This grade generally corresponds to copper concentrates produced from sulfide deposits in Canada.
2. Copper recovery from concentrating would be about 90% of the total contained metal. If nickel was considered, recovery would be around 50%.
3. Recovery in copper extraction would be about 95%, producing a final product containing 97% pure

copper.

4. In order to get the required assumed production, mines and plants would operate year round.

The total quantity of tailings was calculated from the reserve estimate for a conventional smelting operation. The necessary water appropriations were assumed by comparing similar operations of this type. This comparison was done from available literature and communications.

The last group of calculations are regarding estimated cost of air pollution recovery systems. Compared to sulfur recovery, the cost of particulate recovery was assumed negligible. Other assumptions include:

1. Sulfur content in the crude ore was assumed to be about 10% and all of this sulfur would be retained in the concentrate.
2. Since no local market is readily available for sulfuric acid, then the sulfur will have to be recovered as elemental sulfur.
3. From market quotations, it was assumed that elemental sulfur could be sold for \$15/long ton.
4. The cost of recovery was based on the Citrate Process being studied by the Bureau of Mines. They estimate that elemental sulfur can be recovered from the stack gases at a cost of \$35/long ton sulfur when the sulfur oxides are present in low concentrations (less than 4% SO_2)[8].
5. When sulfur oxides are present in higher concentrations (greater than 4% SO_2), then their recovery should be somewhat cheaper. A cost of \$28/long ton of sulfur was assumed.

APPENDIX V: PYROMETALLURGICAL EXTRACTION – TRADITIONAL METHOD

Most of the world's base metals are extracted from their ores and concentrates by pyrometallurgical treatment. This process traditionally includes three sequential operations: roasting, smelting, and converting. The operations are briefly summarized as follows:

1. Roasting: Sulfur is driven off as sulfur dioxide with minor amounts of other sulfur oxides and the iron is oxidized. This step is only necessary when excessive amounts of sulfur are present.
2. Smelting: The roaster product is melted with a siliceous flux that combines with the gangue minerals to form a molten silicate slag and a solution of molten sulfides.
3. Converting: The remaining sulfur is driven off and the remaining iron is oxidized and fluxed for removal as a silicate slag.

Roasting

Roasting is a process where sulfide concentrate containing an above average sulfur content is heated in air (which may be enriched with oxygen) to a temperature at which oxygen combines with the sulfur to form sulfur dioxide and with the metal to form metallic oxides. The amount of sulfur removed is regulated by the amount of oxygen and the furnace temperature. This must be controlled because sufficient sulfur must remain to produce the desired grade of matte. There are three types of roasters. The multi-hearth roaster is the oldest. Due to the relatively long time required in roasting, it has largely been replaced by fluid bed roasters. The third type, the sintering machine roaster, is used to agglomerate the concentrate for smelting in a blast furnace. Figure 5 shows a cutaway view of a fluid bed roaster.

Smelting

Ores and concentrates are smelted either in blast furnaces or reverberatory furnaces. In the blast furnace, the ore is mixed with the fuel and burned by blowing air through the mass. Traditionally, this type of furnace was used for massive sulfide lump ore. Flotation concentrates replaced direct smelting ores as the rich deposits became exhausted. To be used in the blast furnace, these concentrates must be agglomerated to eliminate excessive dust losses. In reverberatory smelting, the ore and fuel are kept separate, and the ore is melted by hot gases which pass over it. With this furnace, fine concentrates can be used as feed without sintering. Consequently, the reverberatory furnace has largely replaced the blast furnace.

Today, because of air pollution control problems with the reverberatory furnace, the blast furnace is being reconsidered. The blast furnace is discussed further in Appendix XIV.

Most ores are difficult to fuse alone and do not develop

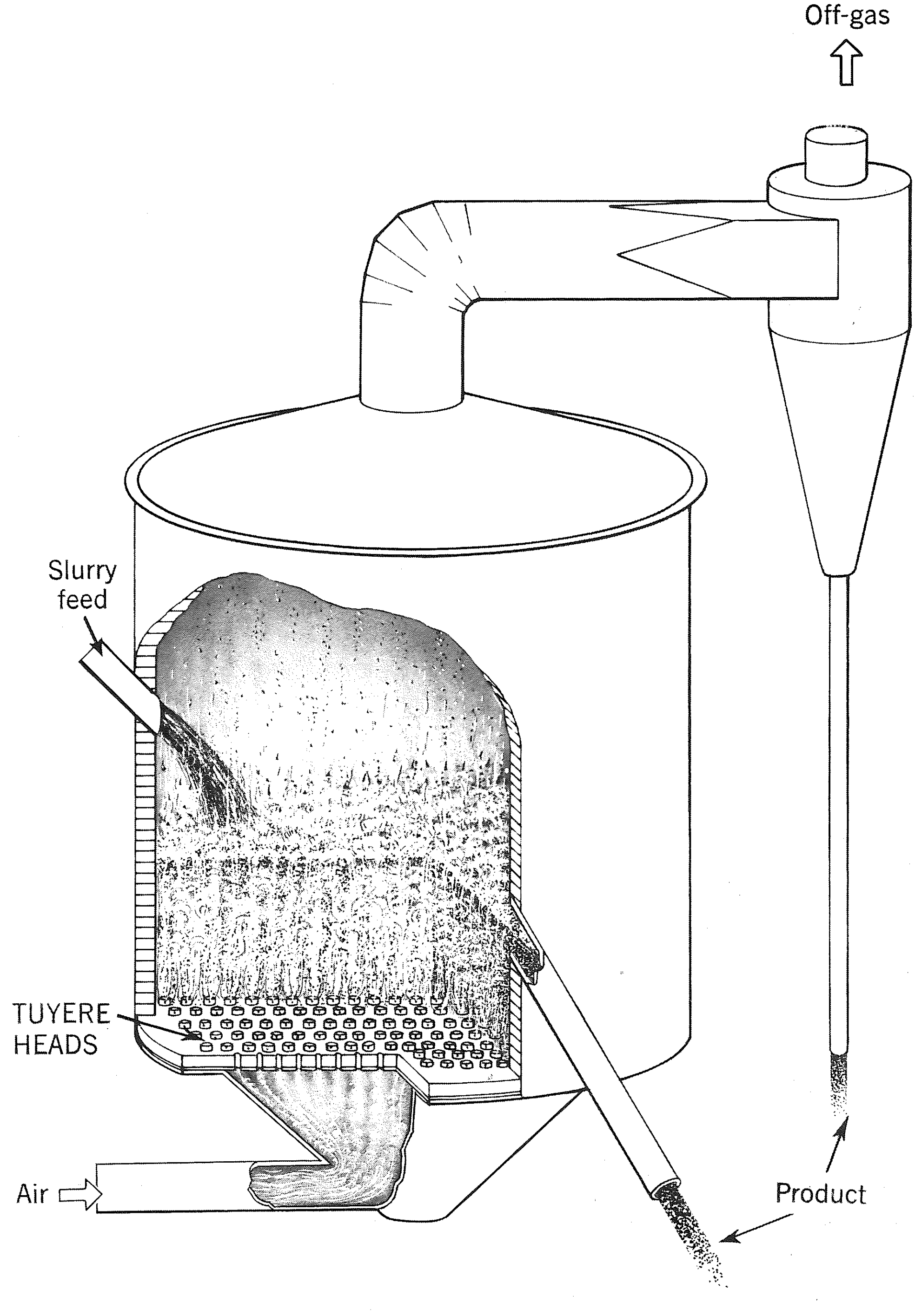


Figure 5 Cutaway View of a Fluid Bed Roaster[6]

sufficiently fluid slag to allow quick, thorough, sulfide concentration. For this reason, a flux is usually added. If the ore is basic, an acid flux, such as silica, is added. If the ore is acid, a basic flux, such as limestone, is added. The three elements of the charge are then proportioned (fuel, flux, and concentrate), so as to obtain the highest metal concentration with the least amount of fuel and flux.

Reverberatory furnaces are used to produce matte. Matte is defined as a complex artificial metallic sulfide. The main constituents are sulfur, copper, iron, lead, nickel, and small amounts of some additional secondary metals. The residual or remaining slag contains the valueless constituents of the ore and is drawn off the top of the molten bath. Not all of the sulfur remains in the matte. A portion of it passes into the flue as sulfur dioxide gas and a small portion of this is converted to sulfur trioxide.

At the high temperature of a smelting furnace, copper, nickel, and other precious metals have an affinity for sulfur. Therefore, these metals will combine with enough sulfur to convert all the copper and nickel to sulfides. Any sulfur remaining will combine with other metals, particularly iron, or be lost to the atmosphere. If there is a large excess of sulfur in the ore, then some will be roasted off prior to smelting. This helps to eliminate dilution of the matte by large quantities of iron sulfide. If the matte is made too rich, some of the copper will be lost. Generally, a matte of 45% to 60% metal is sought.

Reverberatory furnaces (Figure 6) that treat unroasted concentrates produce a steady flow of gases having a very low concentration of SO_2. This concentration can be less than 1% of the total gas volume. Acid plant technology requires a minimum of 4% SO_2 concentration in the offgases for sulfuric acid manufacture. Recovery of the low SO_2 concentrations produced in the reverberatory furnace is at this time unfeasible both technically and economically by available processes.

The operation of the reverberatory furnace is a batch process and thus only one or two charges of ore are treated at a time. The chemical reactions that occur are as follows:

$$9\ NiO + 7\ FeS \rightarrow 7\ FeO + 3\ Ni_3S_2 + SO_2$$

$$Cu_2O + FeS \rightarrow Cu_2S + FeO$$

As mentioned earlier, hot air and gases are blown across the top of the charge and thus fine material can be treated effectively. The charge must be agitated to ensure good fusion.

Converting

A major objective is achieved in the reverberatory furnace: All of the rock and most of the iron is removed. The matte is a complex homogeneous melt containing nickel, copper, iron, and sulfur, plus small amounts of other base elements. The converting process consists of oxidizing the sulfur and iron by blowing a strong blast of air through the molten matte. This produces metallic copper, nickel, and other precious metals. The heat generated keeps the charge fluid. The sulfur is given off as sulfur dioxide, and the ferrous oxide combines with a silica flux to form a slag. Converting is also a batch process and produces intermittent quantities of high concentrations of SO_2 gases. Figure 7 shows a cutaway view of a side blown converter.

APPENDIX VI: HYDROMETALLURGICAL EXTRACTION – LEACHING METHODS

Leaching is a process by which a metal is dissolved from an ore by solvent extraction. The resulting solution is drained from the remaining undissolved rock and the metal is precipitated. Leaching processes are generally divided into three groups: in situ leaching, heap leaching, and confined leaching.

In Situ Leaching

In situ leaching is a method of treating ore bodies containing large quantities of low grade material, without removing the ore from the mine. The material must be highly fractured so that there is a large amount of surface area available for attack by the solvent and so that good circulation is achieved. Action is slow but relatively inexpensive and involves intermittent circulation of air and solution. Sulfide minerals are oxidized during the circulation of air, and the copper oxide formed is removed by the circulating solutions. This process is continually repeated until most of the copper is removed. One problem is that the permeability decreases with time due to slimes and salts that accumulate within the formation.

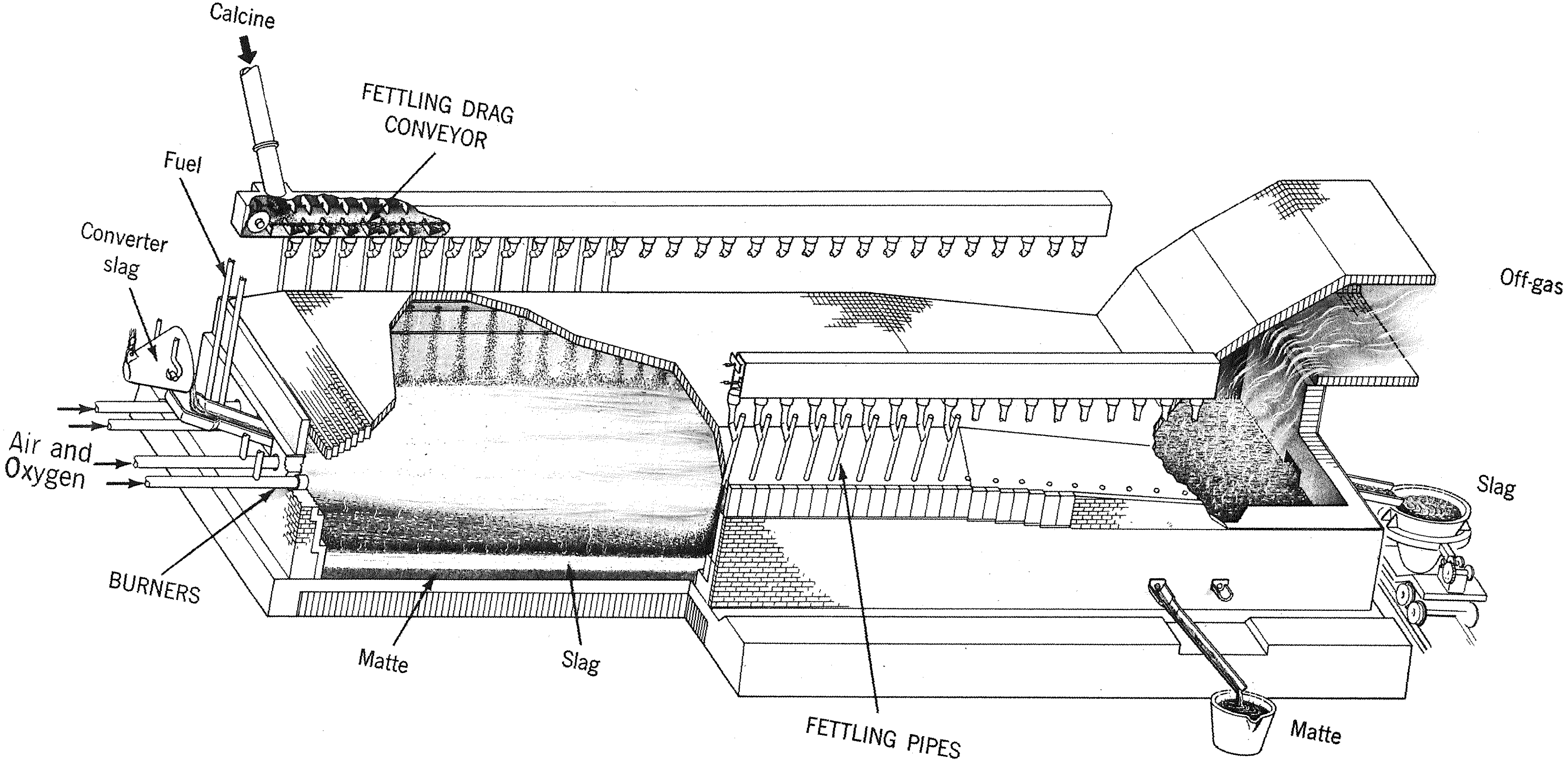


Figure 6 Cutaway View of INCO Reverberatory Furnace[6]

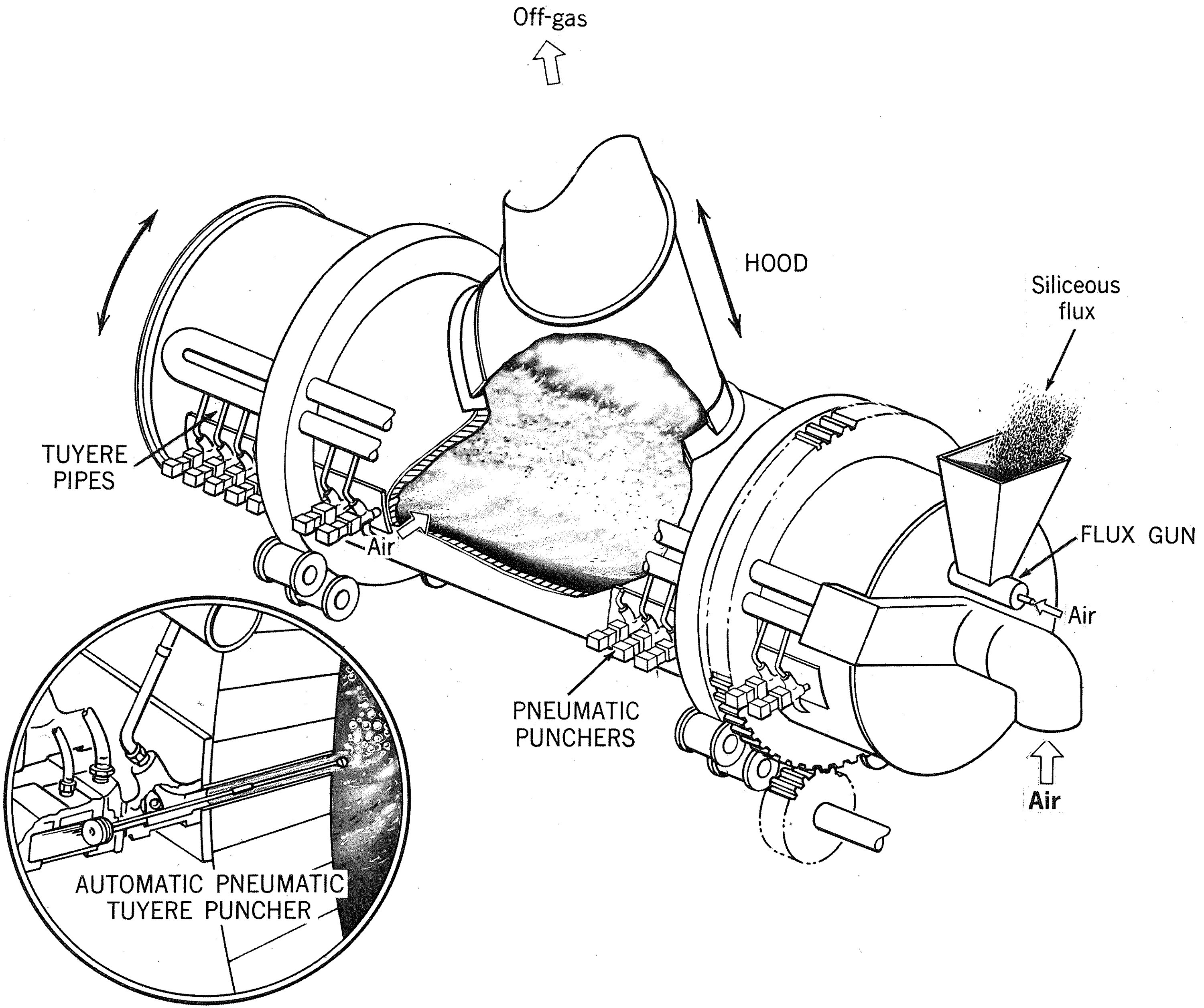


Figure 7 Cutaway View of a Horizontal Side-blown Converter[6]

The copper is accumulated in the circulating solution which is recovered in a collection area at the base of the ore body. Precipitation of copper is usually accomplished by circulating the pregnant solutions through a tank containing scrap iron (preferably tin cans). Iron ions replace the copper ions in solution and cement copper is precipitated[9,10].

In situ leaching would probably not be used in Minnesota because of the low permeability of the formations. Pollution problems associated with in situ leaching are discussed in Appendix XVII.

Heap Leaching

Heap leaching, like leaching in place (in situ leaching), depends on the natural oxidation of the sulfide minerals by intermittent subjection to air and leaching solution. It can be used on oxides, sulfides, or mixed ores. Rock that must be removed from the mine but is too low grade to treat by normal means (concentrating and smelting), can often be heap leached profitably. The basic steps involved are:[11]

A. Selection of Site
    1. Natural terrain with a slight slope
    2. Remove any growth
    3. Waterproof site by rolling or packing with clay or slimes
    4. Drainage is directed to a common point

B. Stockpile the material to be leached

C. Wetting is conducted so that a section of the stockpile is being saturated while other areas are allowed to heat and oxidize.

D. The solutions are collected and the copper is removed as cement copper.

Pollution problems associated with dump leaching are discussed in Appendix XVII.

Confined Leaching

Confined Leaching is accomplished in closed tanks and usually treats relatively high grade material, either ores or concentrates. It was originally used on oxide ores which would leach readily. If a company had a sulfide ore and wanted to leach it, they first had to oxidize the sulfides usually by roasting. New techniques are being considered which would allow direct leaching of sulfide ores and concentrates. These methods are considered in Appendix XV. The basic steps involved in tank leaching are as follows:

A. Reduction to size — The ore is crushed, ground, and screened to size. The necessary fineness depends on:
    1. Porosity
    2. Size of the mineralized grains
    3. Degree of dissemination
    4. Speed with which the mineral is attacked by the leaching solution

B. Roasting of sulfides

C. Depositing the ore in a closed leach tank — in some cases this might be pressurized.

D. Dissolving the copper—Many solvents have been used to dissolve the copper. Sulfuric acid is the most common. Other solvents used are: ammonia, ammonium carbonate, ferric sulfate, sulfurous acid, ferric chloride, cupric chloride, hydrochloric acid, chlorine, and nitric acid. Two principles which should be kept in mind are:
    1. The lower the acid concentration, the less impurities will be dissolved.
    2. In the leaching of copper ores, the necessary time of contact is inversely proportional to the concentration of the solution.

   Example: 8 days of 2.5% acid concentration = 16 days of 1.25% acid concentration

E. Washing — After the copper has been dissolved from the rock and the solution drained off, there is still a large quantity of dissolved copper remaining as entrained solution. This may amount to from 1/3 to 1/2 of the total copper dissolved. Two commonly used methods of removing this entrained solution are:
    1. Fill the interstices with water, circulate and drain. This is repeated until most of the copper is removed.
    2. Fill the interstices with water, draw off at the bottom keeping the material covered and the interstices filled until the draining water shows a negligible quantity of copper. This method is claimed to be the best.

F. Precipitation — There are four methods commonly used to extract copper from the pregnant solution. In the order of their importance, they are:
    1. Electrolysis — This produces very pure refined copper.
    2. Iron Precipitation — The product is an impure

cement copper. The cement copper must then be refined.

3. Precipitation of metallic copper with sulfur dioxide.
4. Precipitation with hydrogen sulfide.

Recently, several other solvents have been evaluated for extracting metals from leach solutions. General Mills has developed organic compounds to be used in metal extraction. The first commercial use of this technology was by Ranchers Development and Exploration Company in Arizona. Bagdad Copper Company has recently built a plant using a similar type of process[12].

APPENDIX VII: REFINING

To improve the quality of the metal, any remaining impurities must be removed by refining.

Three general methods of refining are utilized:

1. Fire Refining: This process produces reactions similar to those which occur in the converter. Iron, lead, zinc, etc. are removed as a silicate slag, and sulfur, antimony, and arsenic are oxidized.
2. Hydrometallurgical Refining: Commonly called electrolytic refining, it is divided into two types: electrorefining and electrowinning. The basic difference between the two processes is: electrowinning has a net cell reaction ($Ni_3S_2 \rightarrow 3Ni + 2S$), whereas, electrorefining has none (Cathode reaction $Ni^{++} + 2e^-$).
3. Vapometallurgical Refining: This process is based on a reaction of the metals with carbon monoxide at atmospheric pressure.

In several cases, refining has already been discussed as part of a specific extraction method.

APPENDIX VIII: DUST RECOVERY

Small particles of material treated in the reverberatory furnace, roaster, and converter are carried up the stacks as suspended particulants. This dust contains valuable metal and is also a serious air pollution problem. There are several types of equipment used for dust recovery. These include: cyclones, scrubbers, electrostatic precipitators, and bag houses.

Cyclones employ the centrifugal principle to remove dust particles. The recovery efficiency ranges from 75 to over 95% for the larger dust particles. However, much of the very fine material still needs removing.

Scrubbers are units in which dust particles contact a liquid, they can then be removed as a slurry. Efficiency in scrubbers varies from 75 to over 99%.

In electrostatic precipitators, solid particles in the offgases are given a charge. They can then be collected by a device carrying the opposite charge. This type of collection is a more costly method; however, efficiencies over 99% can be reached.

Bag houses are units in which the dust-laden offgases are passed through woven cloth which screens out the dust. This method can be over 99.9% efficient.

From the literature, it appears that bag houses and electrostatic precipitators are the most widely used. The added efficiency gained is probably not economic, but is being forced by stringent pollution regulations[6].

APPENDIX IX: EFFECTS OF SO_2 IN THE ATMOSPHERE

The Public Health Service of the Department of Health, Education, and Welfare recommends that SO_2 in the atmosphere in populated areas should not exceed an average of 0.1 parts per million (ppm) parts of air, more than 1% of the time, over a 24-hr. period. Minnesota's air quality standards call for a maximum annual arithmetic mean of 0.02 ppm, a maximum 24-hr. concentration of 0.1 ppm, not to be exceeded more than once per year, and a maximum 3-hr. concentration of 0.25 ppm by volume not to be exceeded more than once per year. Three kinds of sulfur dioxide damage have been found: corrosion, plant damage, and effects on the human body.

Corrosion

Sulfur dioxide in the presence of water produces sulfuric acid which causes corrosion rates to increase. A research program was undertaken to determine the effects of various weak concentrations of sulfuric acid on metal. The solutions varied from 1 Normal to 1/10,000 Normal sulfuric acid (1 Normal = 1 equiv. wt./liter of solution). The metals which were tested include: stainless and nonstainless steel, copper, tin, lead, nickel, zinc, aluminum, cadmium, and chromium. All of the metals tested were affected by corrosion in varying degrees, but stainless steel was found to be most resistant[13]. Near the ASARCO smelter in Tacoma, Washington, SO_2 causes corrosion of paint (particularly automobile paint), metals, stone work, and slate[14].

Plant Damage

Plant damage is thought to be caused by SO_2, or sulfuric acid which has resulted from SO_2. Plant damage is in the form of bleached spots, bleached areas between veins, bleached margins, chloroses, suppression of growth, early abscission, and reduction in yield. For some sensitive plants (rose bushes), the threshold of SO_2 is an atmosphere containing 0.1 to 0.2 ppm SO_2 for a few hours. Sulfur dioxide in combination with very small quantities of ozone (0.03 ppm) appears to result in severe plant damage[15].

Effects on Man

Periods of high SO_2 concentration in urban areas are usually accompanied by other serious pollutants (coal dust, fly ash, etc.). Areas where large amounts of these pollutants exist for short periods of time show higher death rates and higher hospital admissions. Studies of episodes occuring in London suggest that a rise in the daily death rate occurred when the concentrations of sulfur dioxide rose abruptly to levels at or about 715 micrograms/cubic meter (9.25 ppm) in the presence of smoke at 750 micrograms/cubic meter[16].

Many research programs have been undertaken on various kinds of test animals[17]. One such research program is being conducted by Hazelton Laboratories, Inc., and being financed by Edison Electric Institute. The purpose of the program is to provide a scientific base for regulatory limitations designed to protect humans from combustion products emitted by power station stacks.

Four groups of thirty guinea pigs each were exposed to sulfur dioxide for one year. The groups were as follows:

Group 1	0.1 ppm SO_2
Group 2	1.0 ppm SO_2
Group 3	5.0 ppm SO_2
Group 4	0.0 ppm SO_2

Their lungs were tested periodically for elasticity, airflow resistance, breathing effort, and diffusion of oxygen and carbon dioxide. The groups exposed to the lower concentrations indicate no physiological or mechanical damage. Exposure to the maximum SO_2 concentration enhanced the lung's ability to diffuse oxygen and carbon dioxide. Blood tests disclosed no ill effects on the animals. Even with the 5 ppm exposure on guinea pigs, results showed no deleterious effects on any vital organs. The SO_2 actually lowered their susceptibility to pulmonary disease and enhanced their survival rate. Post-mortem revealed less than usual pathological change in the animals' kidneys. However, because laboratory work of this type generally does not simulate the actual environment, the results should only be used with great caution.

APPENDIX X: AIR POLLUTION POTENTIAL

The present National Weather Services' Air Pollution Weather Forecast Program is an outgrowth of efforts begun in the late forties to forecast periods of severe high air pollution potential or air stagnation. "Air Stagnation" is defined as a measure of the inability of the atmosphere to adequately dilute and disperse pollutants emitted into it.

Research has shown that broad area homogeneous pollutant concentrations do not ordinarily approach or reach harmful levels until air stagnation conditions persist beyond a 24 to 36-hour period. A highly dependent factor associated with harmful levels is, however, proportionally related to the types, locations, and volumes of the pollutant emissions as much as it is also dependent upon the varying tolerance levels of affected animate receptors. When air stagnation conditions are expected to persist beyond 36 hours (an episode) the National Weather Service issues an "Air Stagnation Advisory" (ASA). The advisory is then continuously updated through the episode period and finally cancelled when weather improves sufficiently to eleviate the incipient condition.

Air Pollution Potential is evaluated according to a number of specific meteorological parameters. These include:

1. Surface wind speeds less than 8 mph

2. Below 18,000 feet, no winds greater than 30 mph
3. Below 14,000 feet, the existence of subsidence "sinking" into the air mass below
4. No precipitation
5. These conditions must exist in an area greater than or equal to 275 square miles
6. Conditions expected to persist at least 36 hours (not a normal case of dirunal night-time pollution buildup and daytime ventilation).

No single parameter produces an episode. All conditions must exist simultaneously and persist for 36 hours. Such weather conditions are produced by a strong, slow moving weather structure called a high-pressure system. A system of this type usually produces a temperature inversion of from 4 to 9°C. Figure 8 shows this type of weather structure and the resulting inversion graph[18,19,21].

A simple equation may be used to demonstrate the general parameters of air stagnation, though more complicated methods and equations are employed by the National Weather Service in actual evaluations and forecasting:

$$V = U\,M$$

V = Ventilation (m^2/sec)
U = Transport Wind Speed (m/sec)
M = Mixing Height (m)

The terms are defined as follows:

1. Ventilation is the measure of the volume rate of horizontal transport of air within the mixing layer per unit distance normal to the wind.
2. Transport wind speed is the measure of the average rate of horizontal transport of air within the mixing layer.
3. Mixing height is the height into which relatively vigorous mixing occurs.

If V is greater than 6000 meters^2/sec, or if U is greater than 4 meters/sec, then any emitted pollutants will not concentrate. A special mixing height must be introduced, called the urban morning mixing height (M_{UM}). If this factor, M_{UM}, is greater than 500 meters, then again, pollutants will not concentrate. Therefore, if any one of the three quantities is greater than their respective values, then there is no air stagnation potential.

The National Weather Service has calculated air pollution potential throughout the United States. These were then plotted in Figure 9 according to the number of yearly episodes. Minnesota is in an ideal position in that we have less than one episode yearly.

In Northern Minnesota then, we must be concerned with an occasional episode and other pollution periods of shorter duration (incidents).

APPENDIX XI: WIND STATISTICS FOR NORTH-EASTERN MINNESOTA

In order to evaluate the possibilities of locating a smelter in Minnesota, a study of wind conditions is necessary. This involves two phases, first, the surface winds must carry the unrecovered gases up into the atmosphere and second, the upper winds must disperse them. This, of course, assumes that smelter recovery systems will remove sufficient gases so that standards can be met.

Surface Winds

The Department of Natural Resources made a study of surface wind conditions using data collected from twenty-one stations in Northeastern Minnesota. The source of information and locations are as follows:

State Land and Forestry Offices

Alborn (10)
Aurora (8)
Cloquet (15)
Cloquet Valley (12)
Cook (3)
Cotton (11)
Cromwell (14)
Duluth (13)
Eveleth (7)
Finland (18)
Floodwood (9)
Hibbing (6)
Hovland (21)
Orr (2)
Tower (4)
Two Harbors (16)

Superior National Forest Offices

Ely (5)
Isabella (19)
Two Harbors (Jordan)(17)
Sea Gull (20)

National Weather Service

International Falls (1)
Duluth (13)

FAA, Flight Service Station

Chisholm – Hibbing (6)

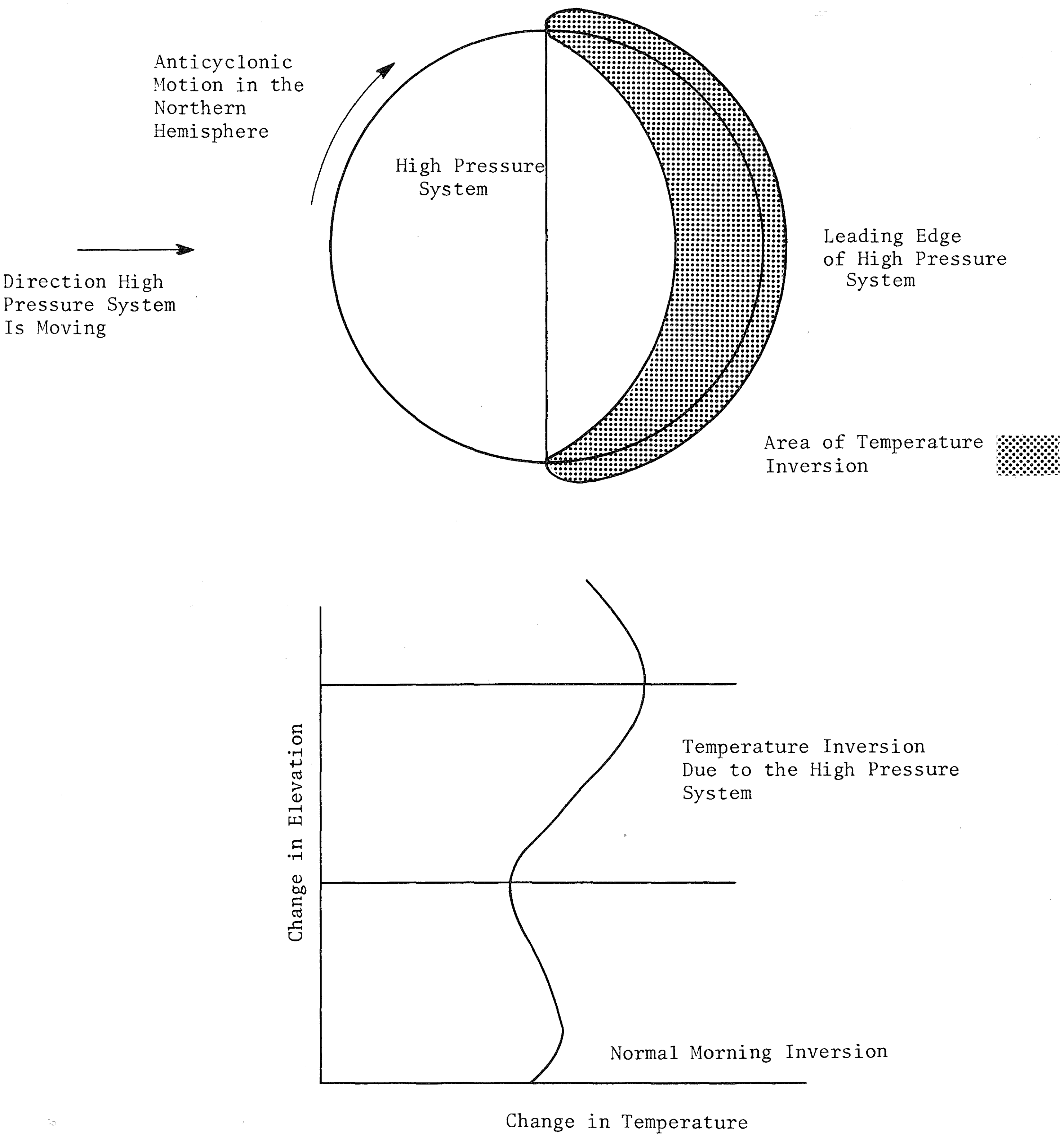


Figure 8 High Pressure System & Temperature Inversion Graph

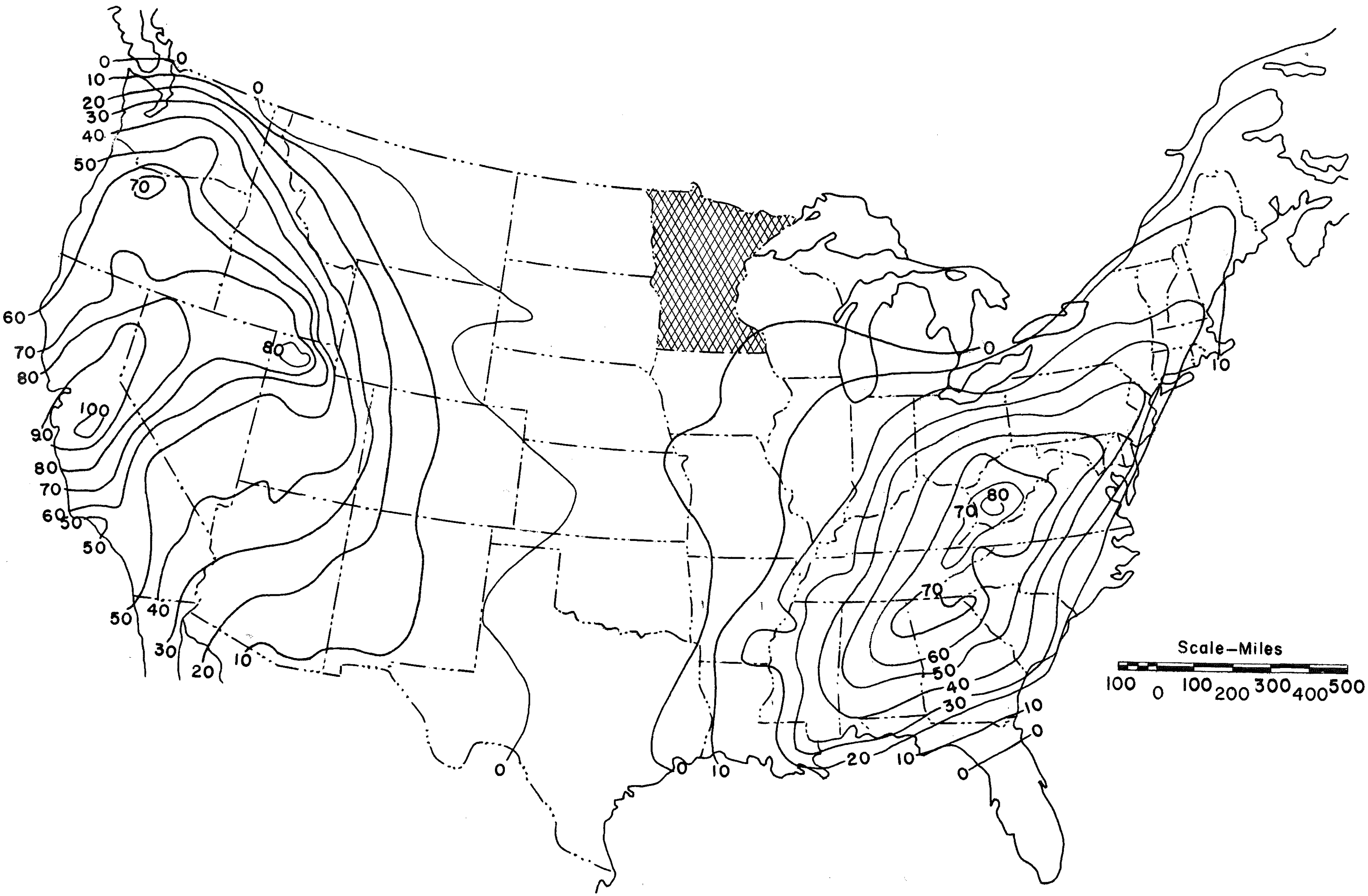


Figure 9 Forecast of Yearly Air Pollution Potential Episodes[16]

Figure 10 shows the location by the corresponding number. Most of the data collected is for a period of one or two years and in the case of forest stations, is for an eight-month period usually from April through October. Figure 11 shows a key to the wind roses and describes the information contained on each data sheet. The wind rose compiled for each station studied is found on the pages following. Although this information is by no means complete, it can serve as a first step in locating a possible plant site. Once an individual site has been selected, a more detailed study should be made.

Another study is currently being made by the Department of Natural Resources on emission from power plants in Northeastern Minnesota in order to see if snowfall will concentrate sulfur from the air. If so, the local wind conditions could be evaluated and areas of concentration detected for a specific sulfur source. Results of this study may be available later after more work has been completed.

Upper Winds

After the off gases have been carried up into the atmosphere, they must be dispersed by the upper winds. These winds are relatively constant and vary only slightly in speed and direction. Mean yearly wind speed generally varies from 12 mph at approximately 5,000 feet, to a maximum of 45 mph in the 30,000 to 40,000 foot range. The mean direction (direction from which the wind blows) shows a relatively small variance of nine degrees, between 279° and 288° (individual directions were added vectorially to find the mean direction). Additional information can be found in Upper Wind Statistics of the Northern Western Hemisphere[21]. Table 3 shows a summary of the upper wind speed and direction. The variance during any one year from the mean wind speed and direction are insignificant.

APPENDIX XII: THE TALL STACK APPROACH

The key to the tall-stack approach is to emit sulfur oxides high enough up into the atmosphere to ensure dispersion of these oxides to acceptable standards before they descend to the ground. A study of the influence of verticle temperature variations on stack effluents is shown in Figure 12.

Research in Great Britain led to the following conclusions:

1. Sulfur dioxide concentrations at any ground level point are very transient and infrequent, and their magnitudes are predictable within a reasonable degree of accuracy.
2. No historical meteorological situation has been encountered in which the short-term peak concentrations are more than double those in neutral conditions.
3. Hot plumes from tall stacks rise high in stable atmospheric conditions and make virtually no contribution to ground level pollution.
4. The higher the stack, the greater the plume rises, and the more frequently will stable layers in the lower atmosphere shield the ground surface.

The height of the stack should be designed 2½ times the height of the surrounding buildings, plus additional height to compensate for the contour of the adjacent land. This procedure, although not a solution, is a good practice once the SO_2 content in the gas emissions has been reduced as much as possible[22].

Table 3. Upper Wind Statistics for Northeastern Minnesota

Elevation in Standard Atmospheres (millibars)	Elevation (feet)	Mean Yearly Wind Speed (mph)	Vector Mean Direction (Degrees Clockwise From North)
850	4,800	12	283
700	9,900	20	288
500	18,400	32	285
300	30,200	45	280
200	38,800	45	279
100	53,500	32	284

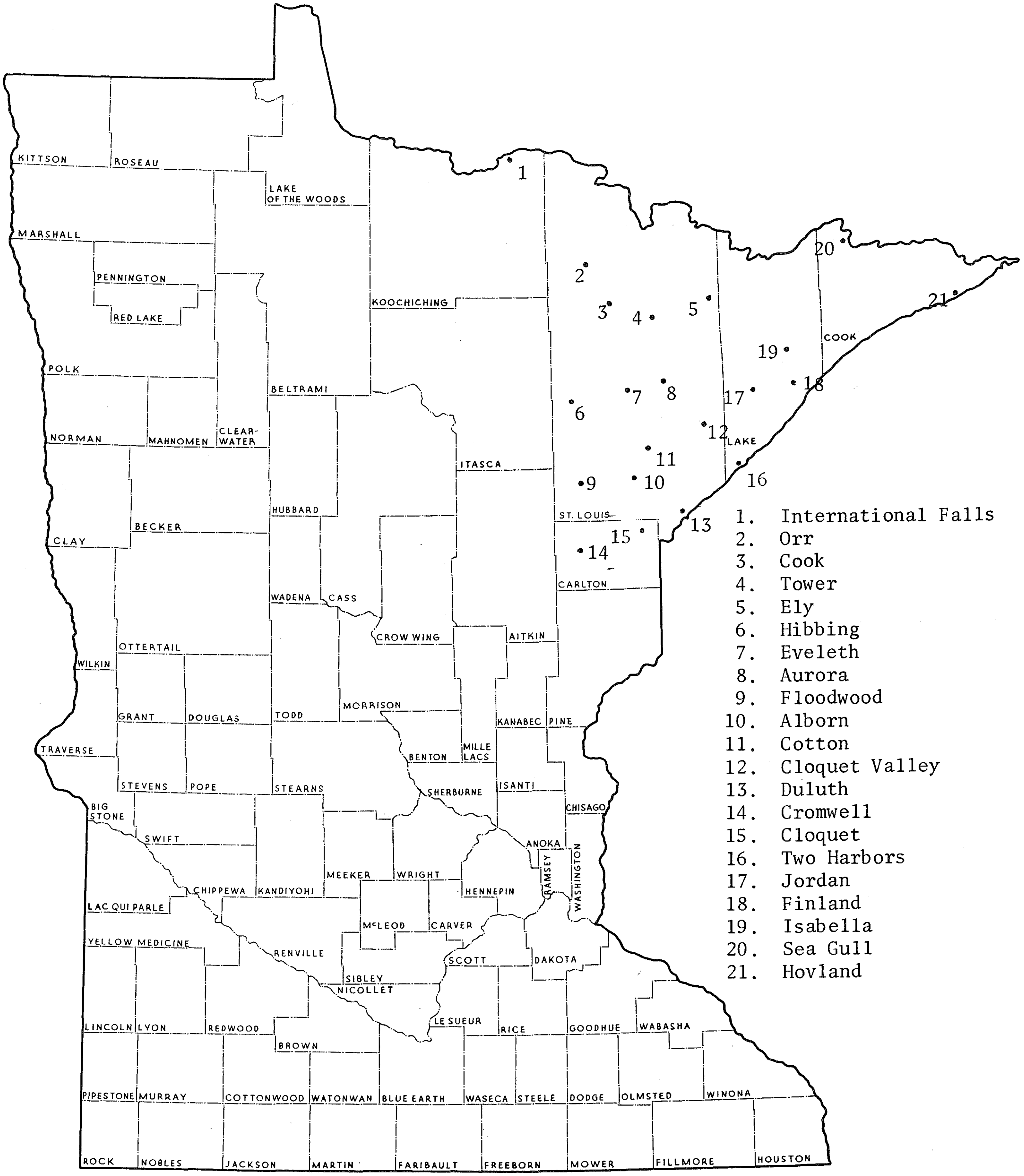
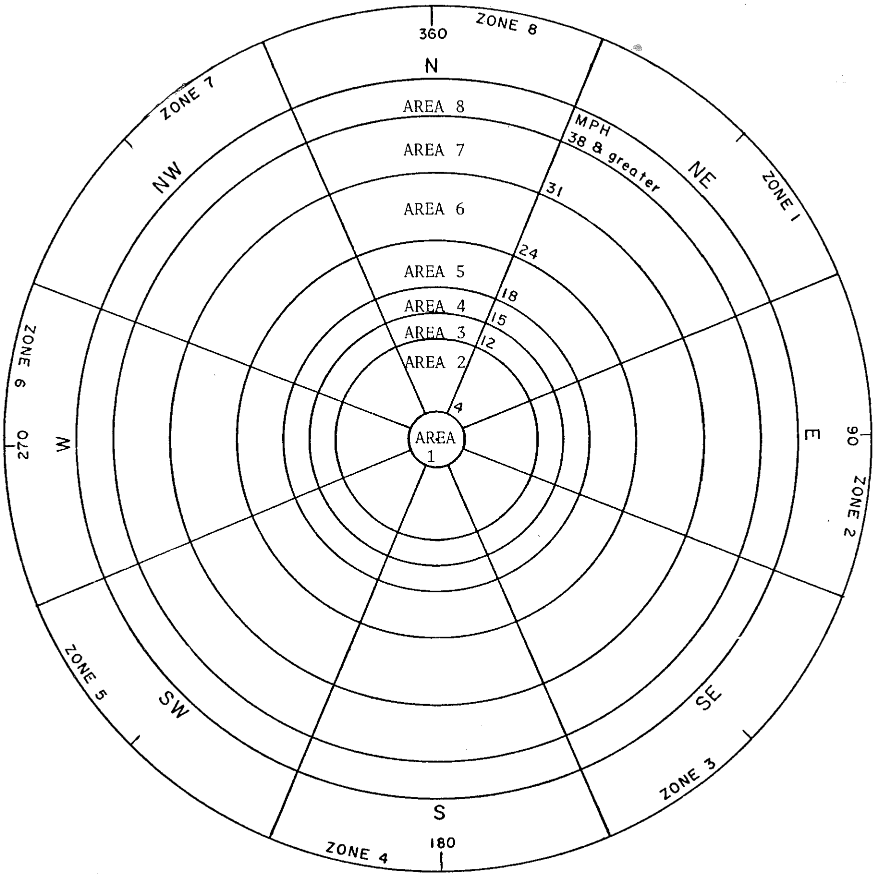


Figure 10 Location Map for Surface Wind Roses

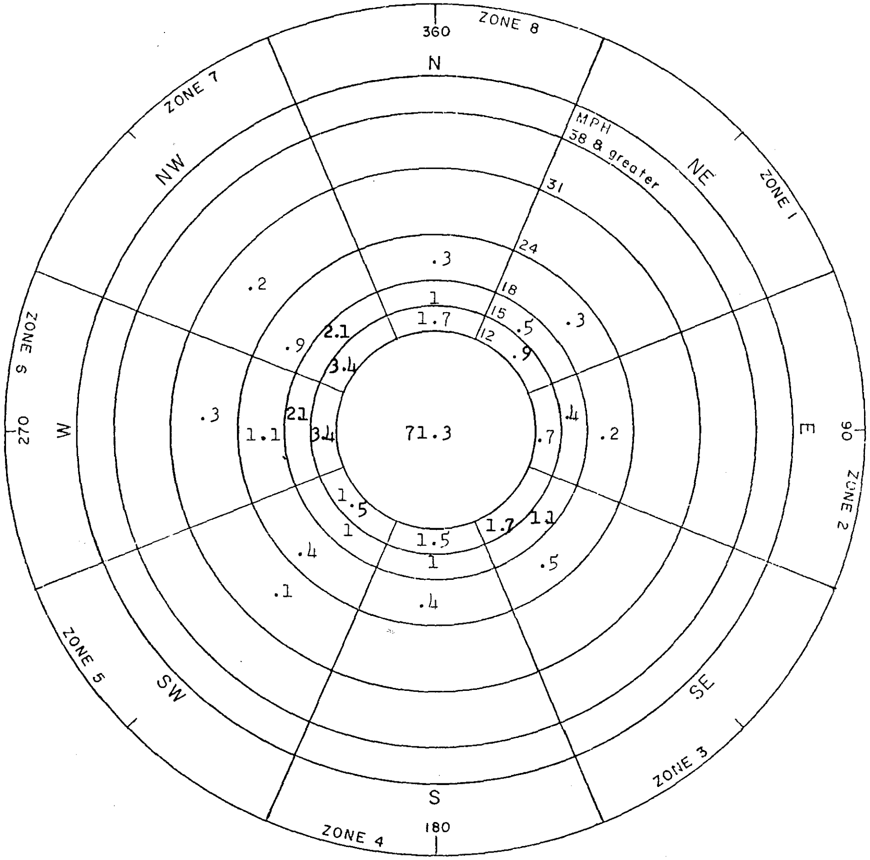


The wind rose is divided into eight equal zones; each one represents the direction from which the wind is blowing. For example, Zone 8 represents wind blowing from the northerly direction. Each rose is further divided into eight radial areas and a perimeter region. The eight areas stand for different wind speeds as follows:

Area	Wind Speed (mi/hr)
1	<4
2	4 – 11
3	12 – 14
4	15 – 17
5	18 – 23
6	24 – 30
7	31 – 37
8	⩾38

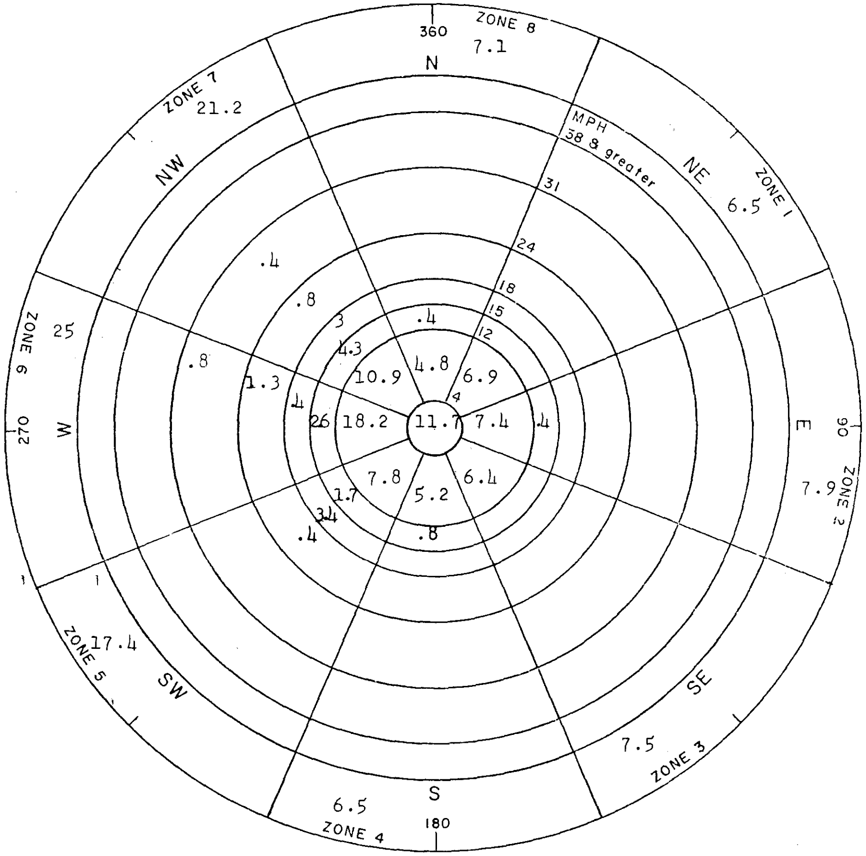
The number in the perimeter region is the percent of the time the wind is blowing for the entire zone. Numbers are expressed as a percentage of the time the wind is blowing in a zone and area.

Figure 11 Key to Wind Rose Data Sheet



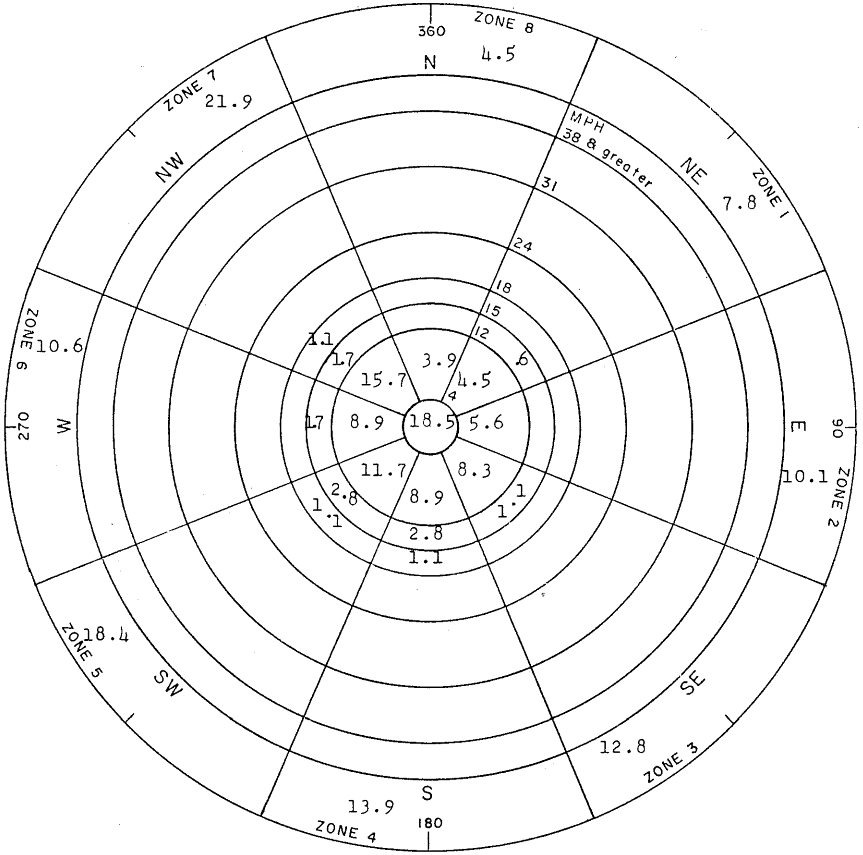
Location: International F-lls, Minnesot- (1)

Wind Data Collected: 3/56 - 2/61



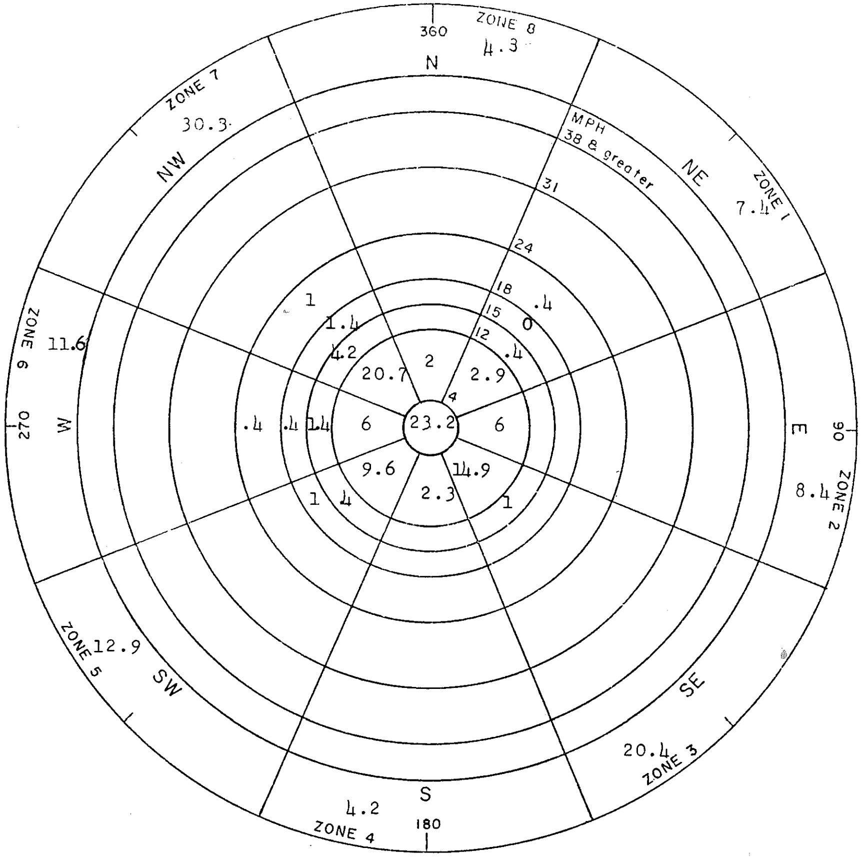
Location: Orr, Minnesota (2)

Wind Data Collected: 4-1-70 to 11-20-70



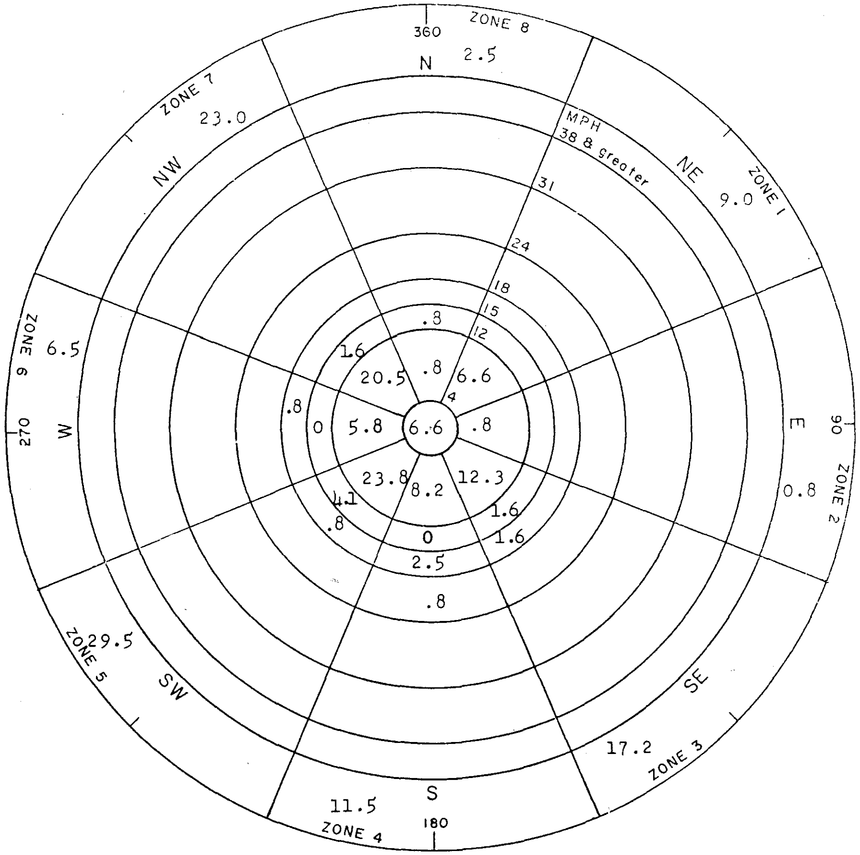
Location: Cook, Minnesota (3)

Wind Data Collected: 4-13-70 to 11-31-70



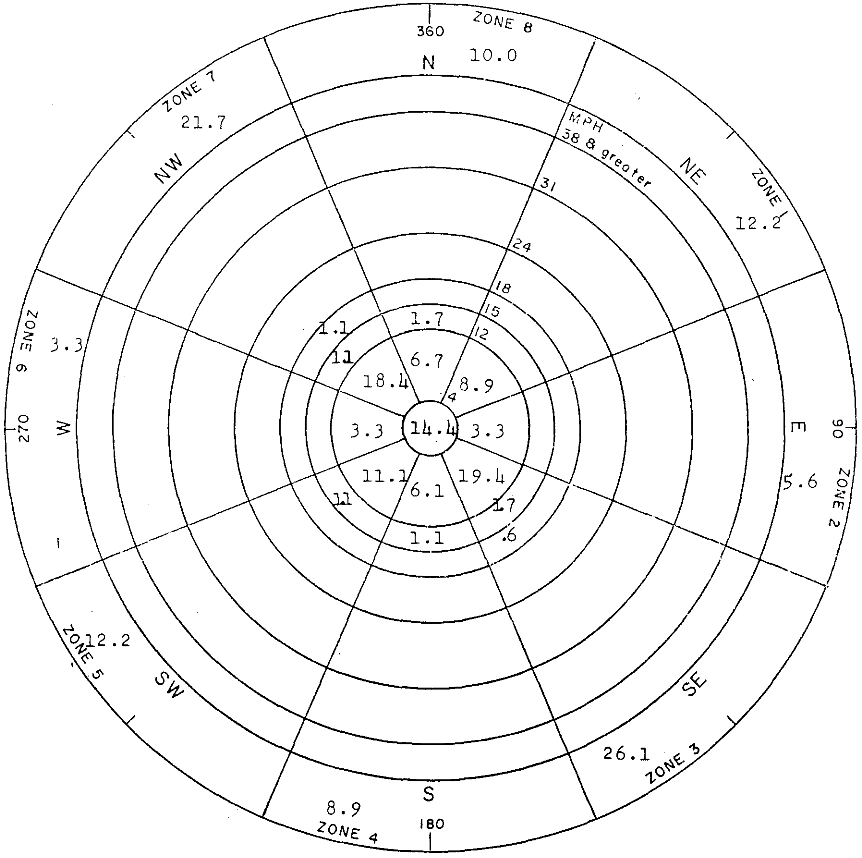
Location: Tower, Minnesota (4)

Wind Data Collected: 4-1-70 to 11-10-70



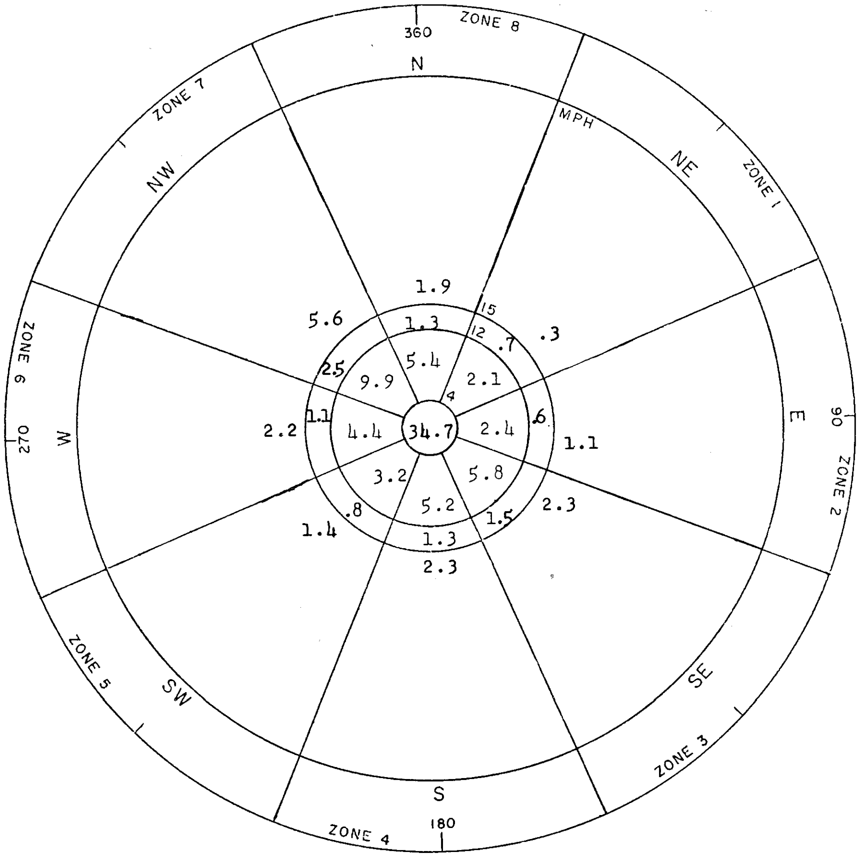
Location: Ely, Minnesota (5)

Wind Data Collected: 7-1-69 to 10-31-69



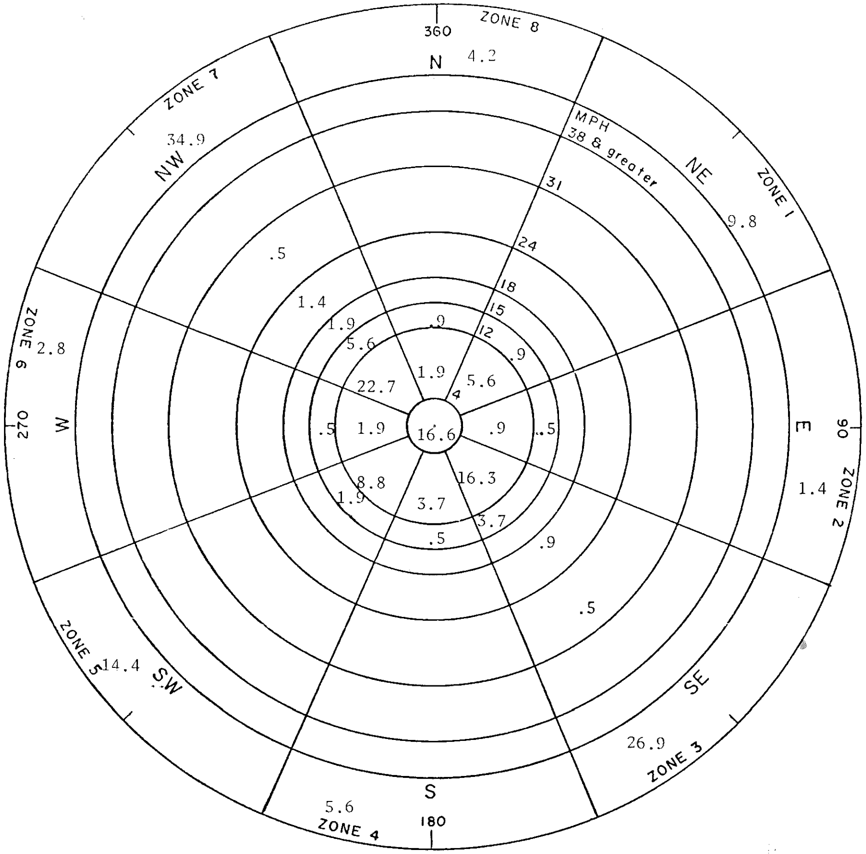
Location: Hibbing, Minnesota (6)

Wind Data Collected: 3-26-70 to 11-7-70



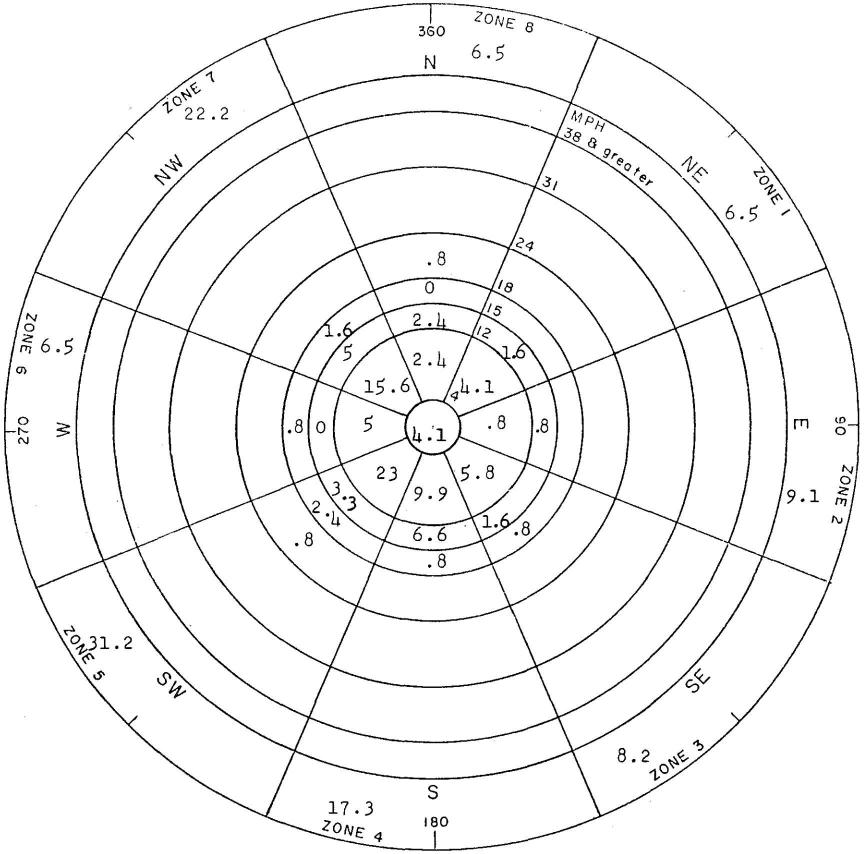
Location: Chisholm-Hibbing Airport, Minnesota (6)

Wind Data Collected: January 1953 - January 1956



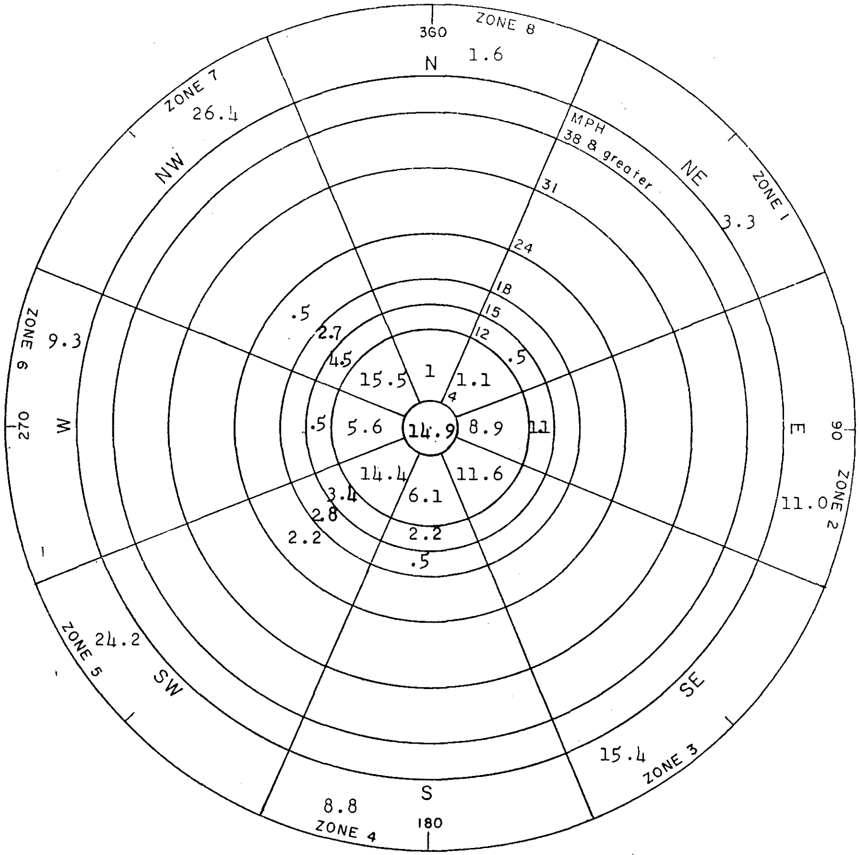
Location: Eveleth, Minnesota (7)

Wind Data Collected: 3-26-70 to 11-7-70



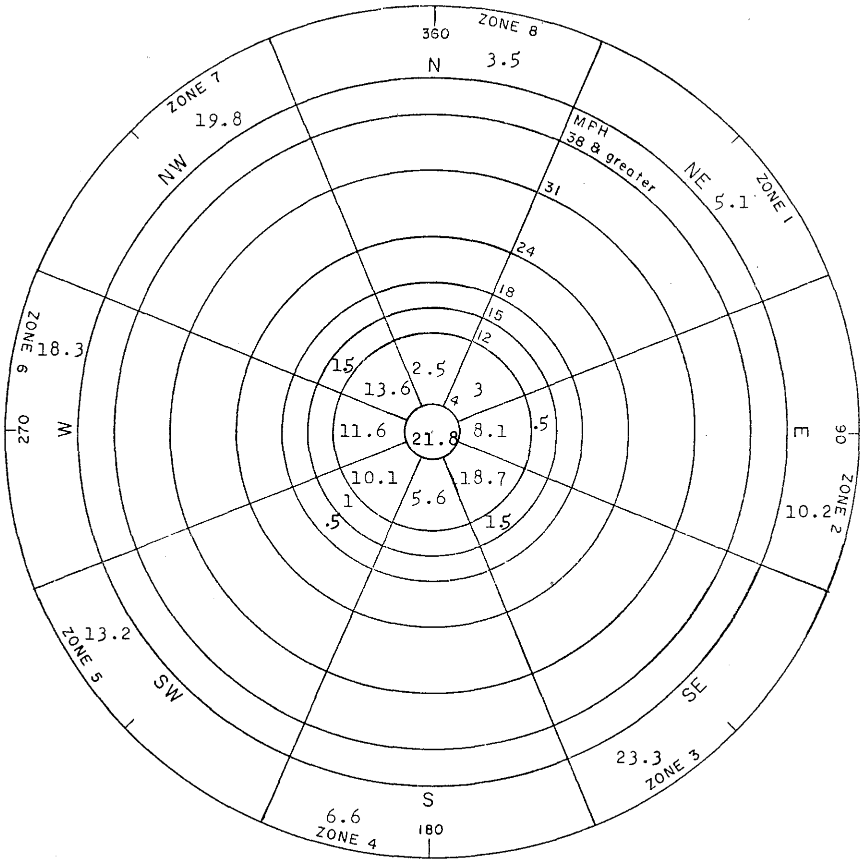
Location: Aurora, Minnesota (8)

Wind Data Collected: 7-1-69 to 10-31-69



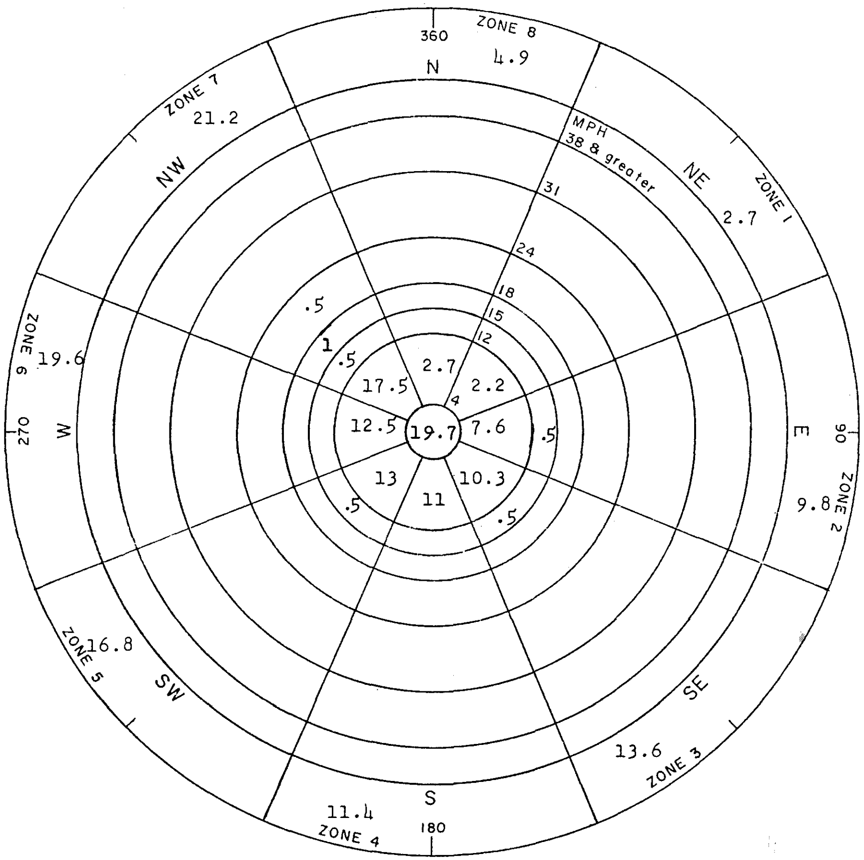
Location: Floodwood, Minnesota (9)

Wind Data Collected: 4-6-70 to 10-29-70



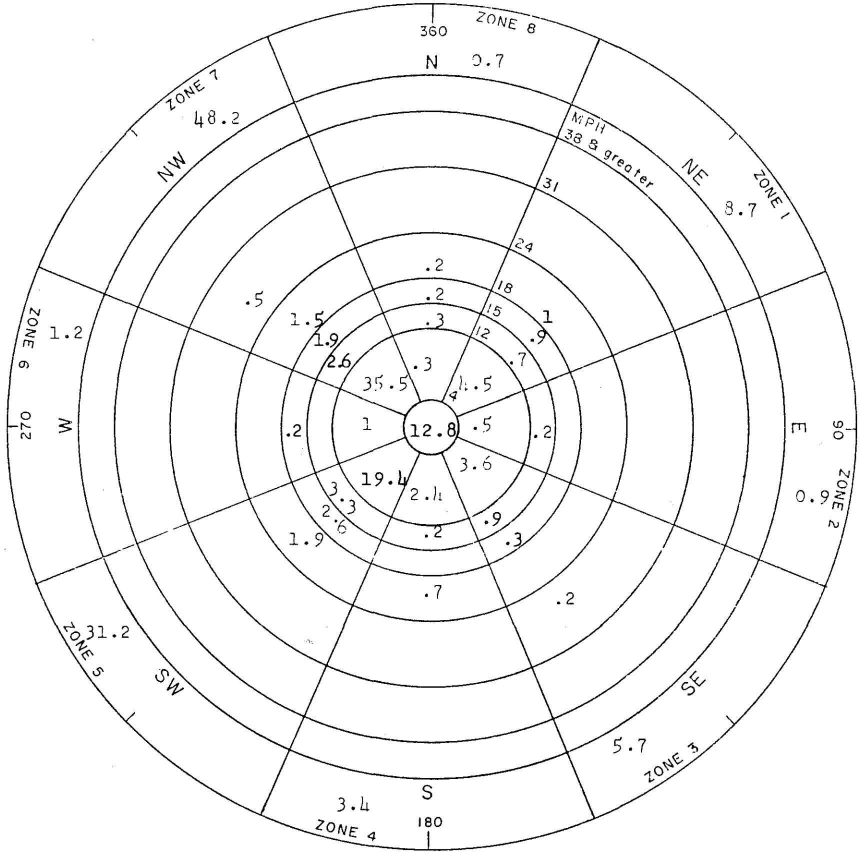
Location: Alborn, Minnesota (10)

Wind Data Collected: 4-1-70 to 10 31-70



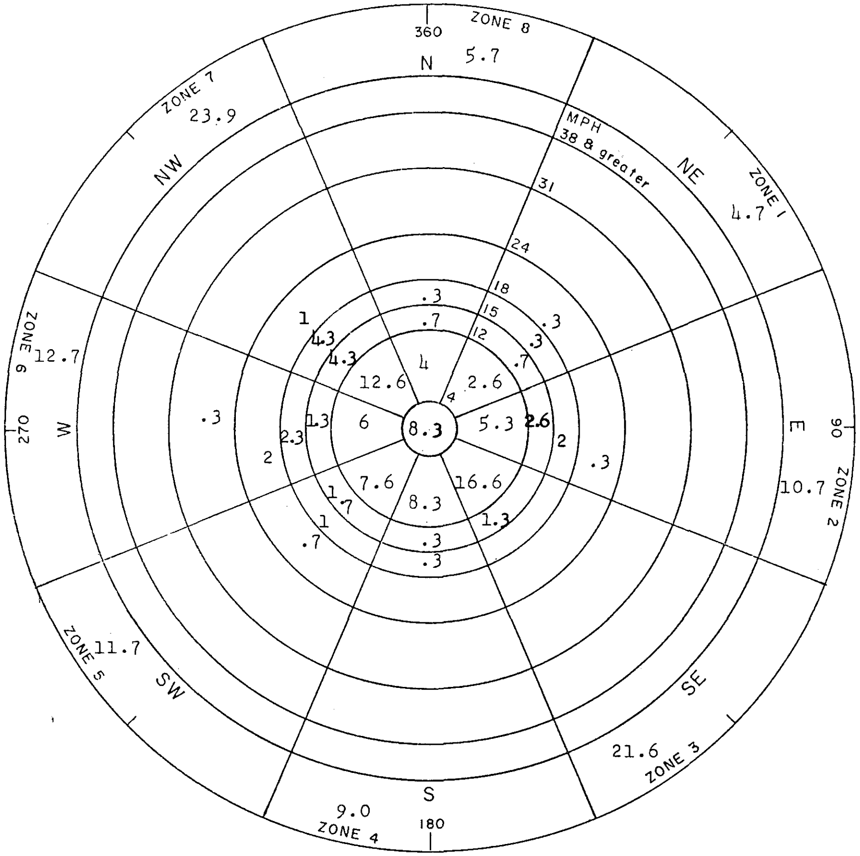
Location: Cotton, Minnesota (11)

Wind Data Collected: 4-1-70 to 10-30-70



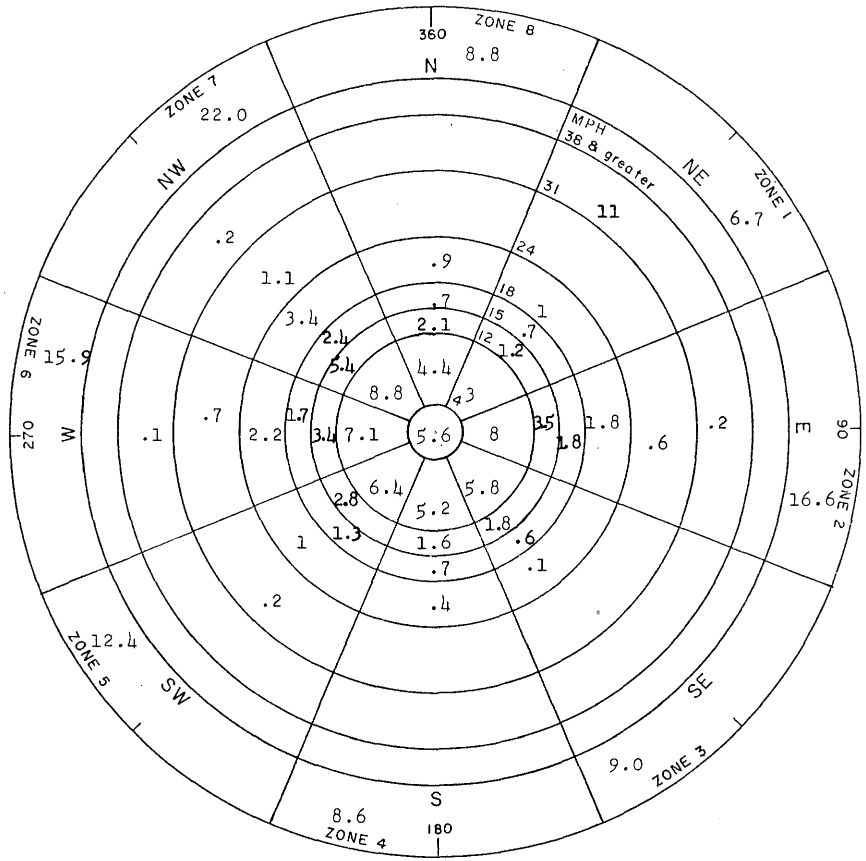
Location: Cloquet Valley, Minnesota (12)

Wind Data Collected: 3-29-68 to 10-31-68
4-11-69 to 10-31-69
4-1-70 to 10-10-70



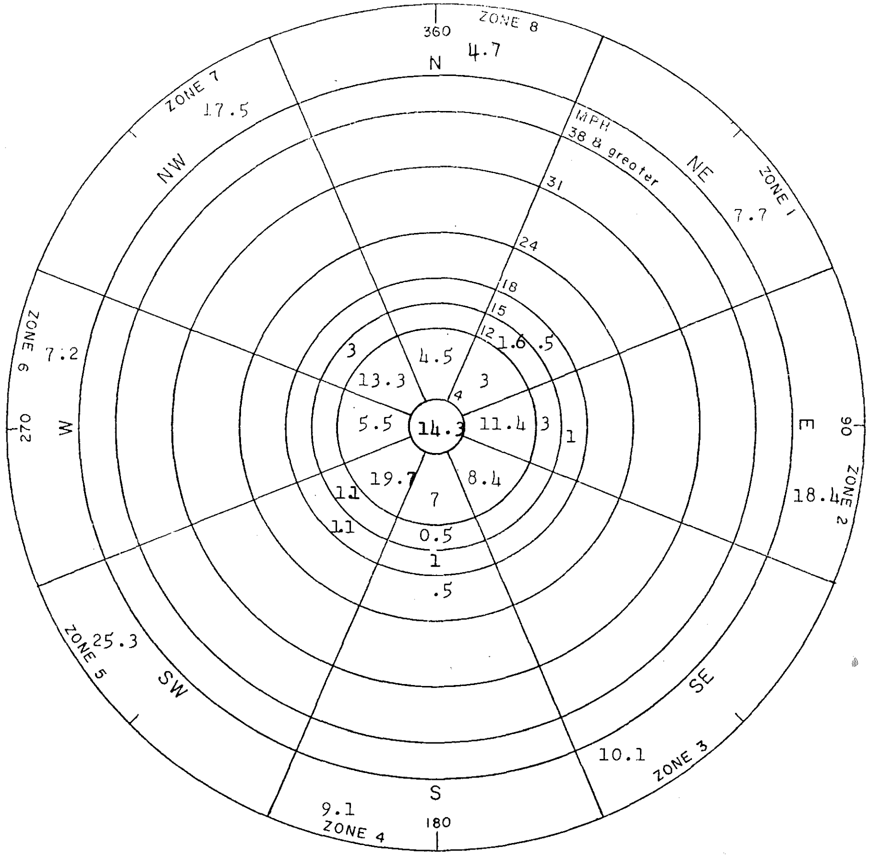
Location: Duluth, Minnesota (13)

Wind Data Collected: 4-1-69 to 11-10-69, 4-1-70 to 10-31-70



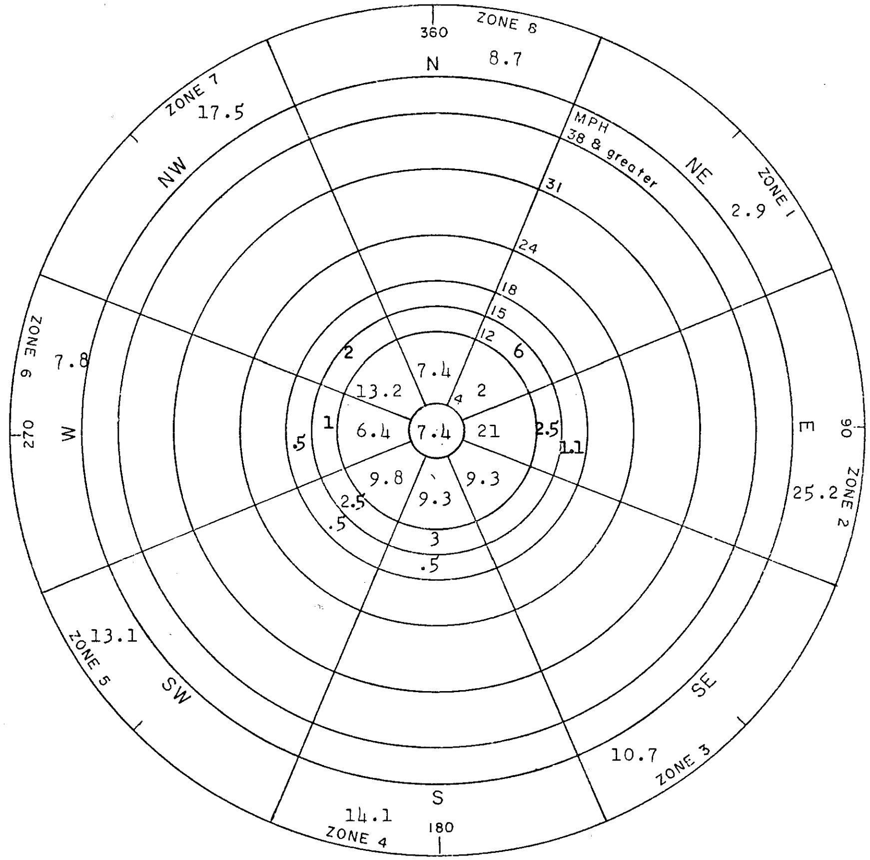
Location: Duluth Airport, Minnesota (13)

Wind Data Collected: 1951 - 1960



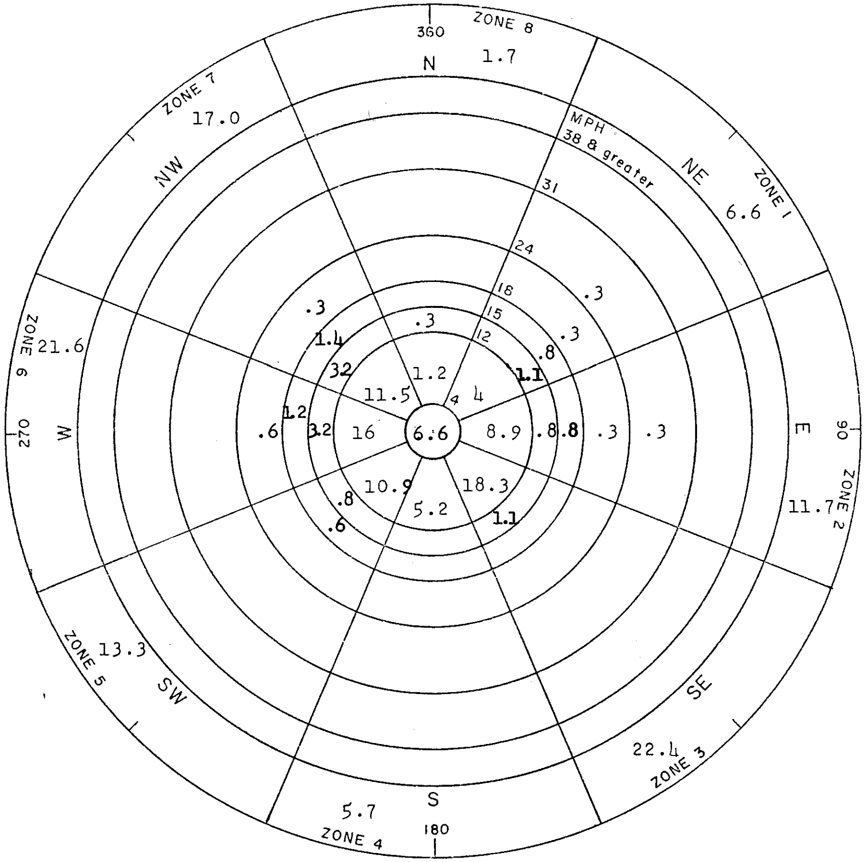
Location: Cromwell, Minnesota (14)

Wind Data Collected: 4-1-70 to 10-31-70



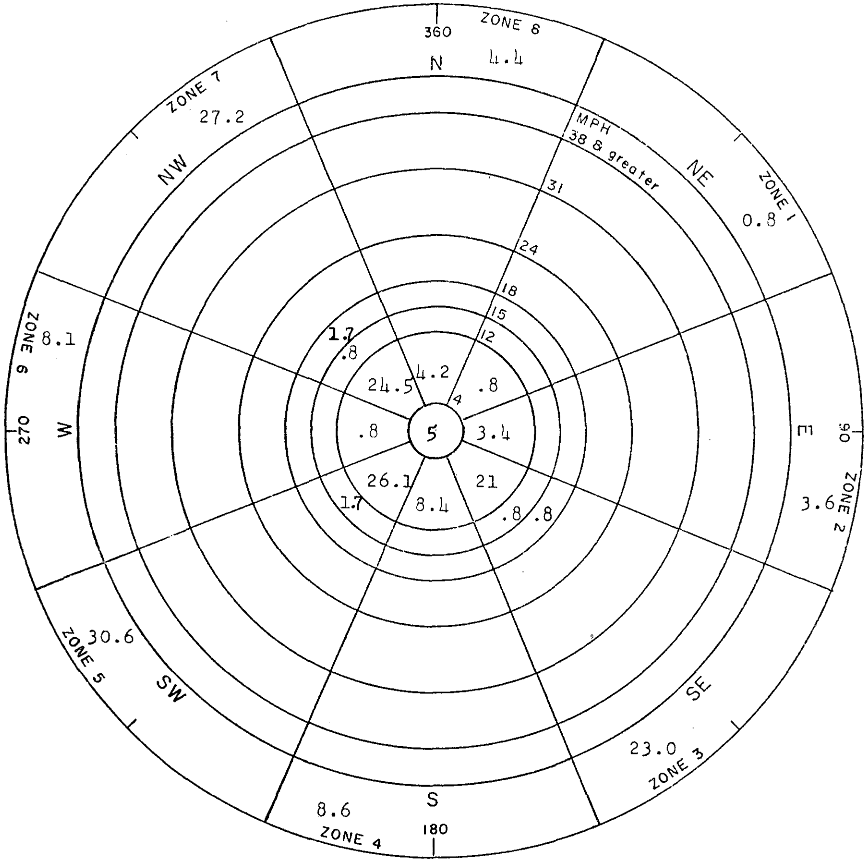
Location: Cloquet, Minnesota (15)

Wind Data Collected: 4-7-70 to 10-31-70



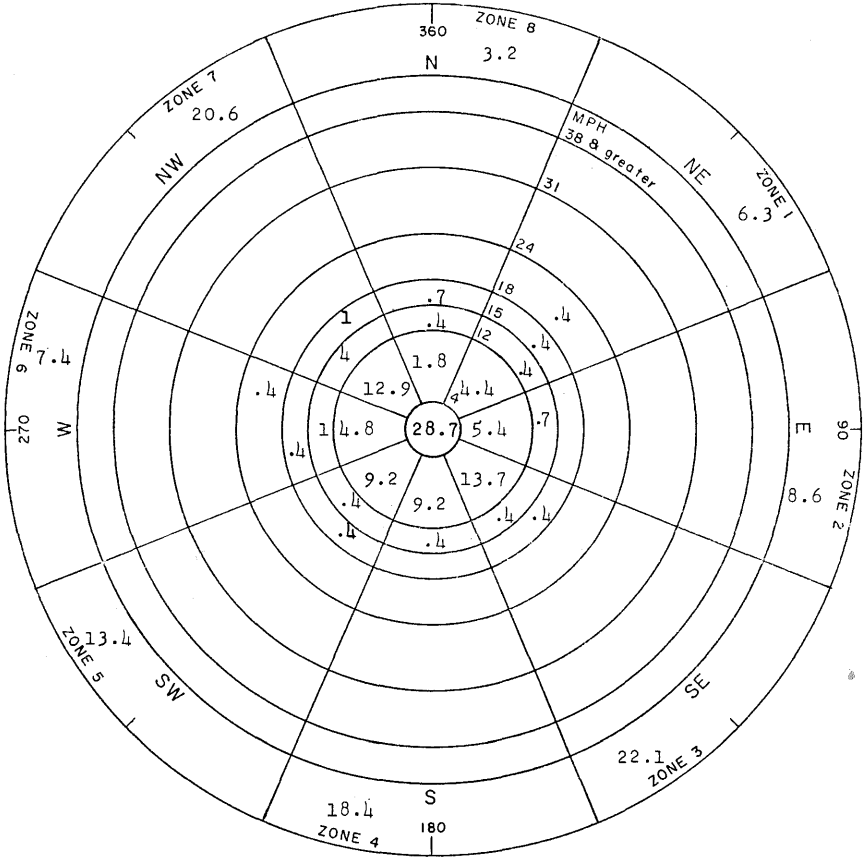
Location: Two Harbors, Minnesota (16)

Wind Data Collected: 4-14-69 to 10-31-69, 4-11-70 to 10-20-70



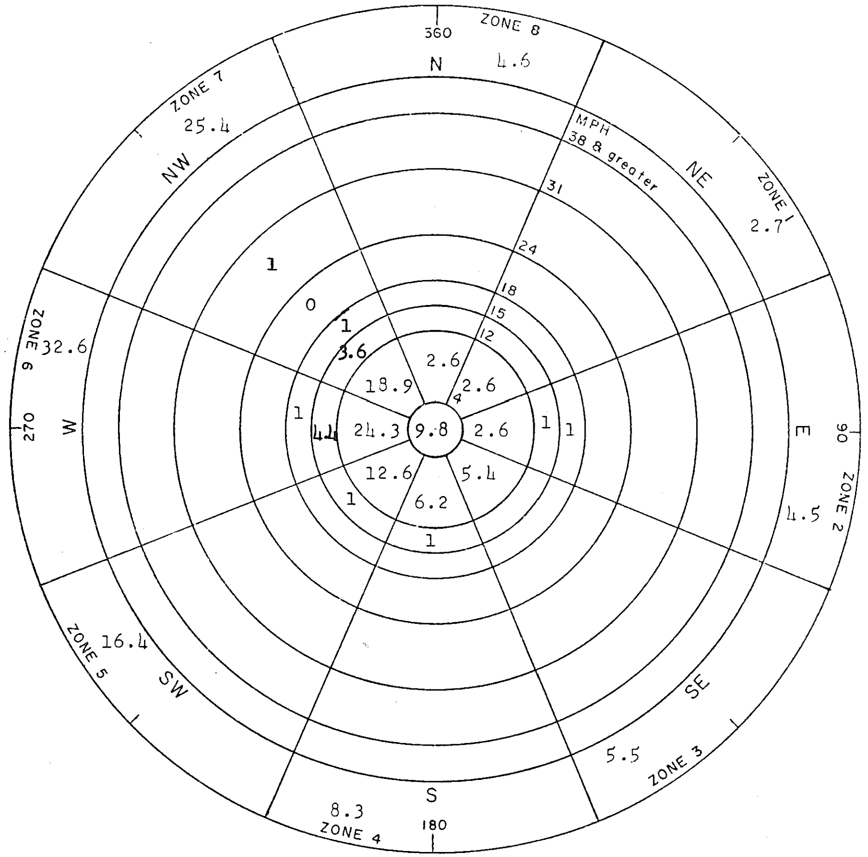
Location: Two Harbors (Jordan), Minnesota (17)

Wind Data Collected: 7-1-69 to 10-27-69



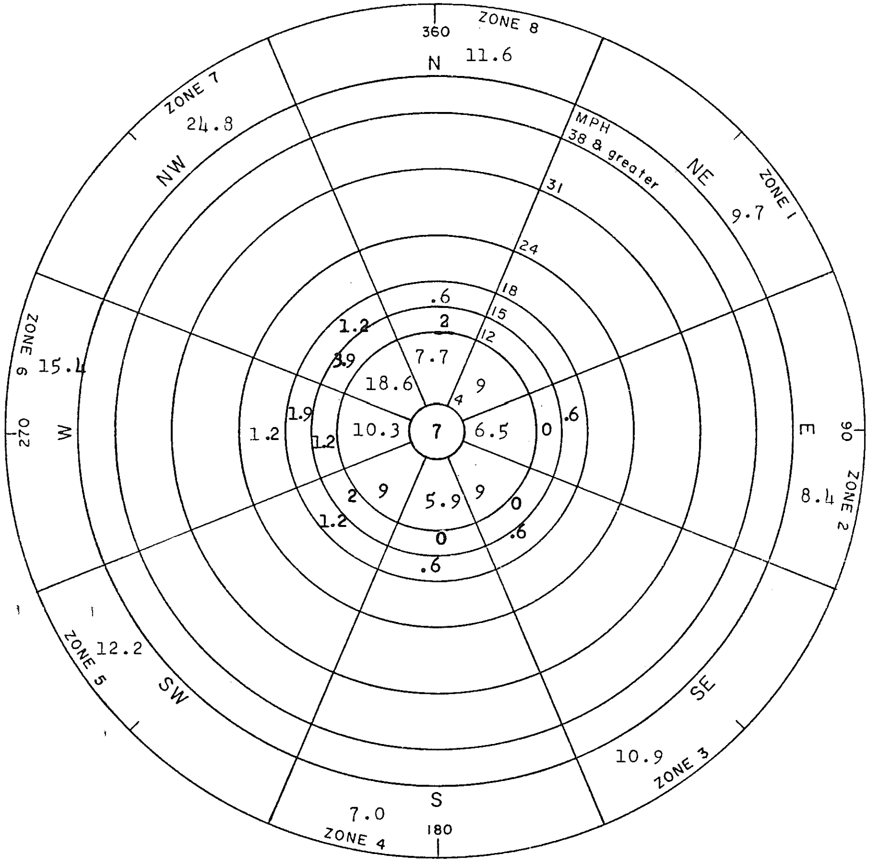
Location: Finland, Minnesota (18)

Wind Data Collected: 4-21-69 to 10-10-69, 4-11-70 to 10-20-70



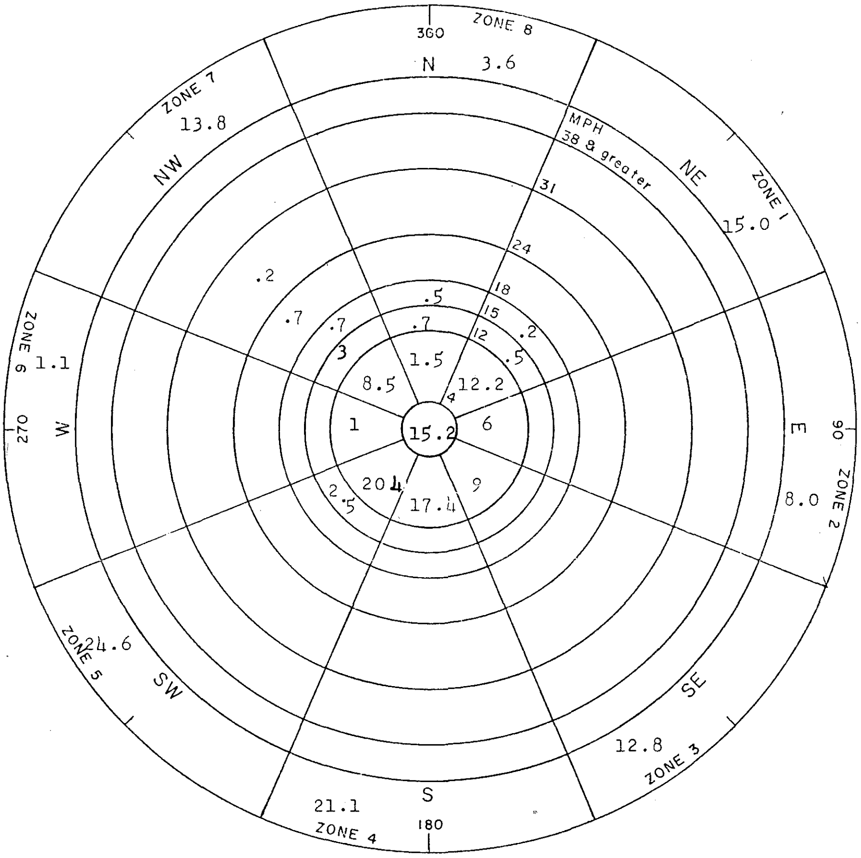
Location: Isabella, Minnesota (19)

Wind Data Collected: 7-1-69 to 10-20-69



Location: Sea Gull, Minnesota (20)

Wind Data Collected: 4-30-68 to 10-24-68

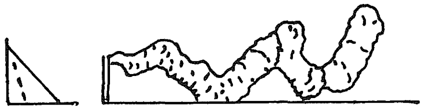


Location: Hovland, Minnesota (21)

Wind Data Collected: 4-1-69 to 10-31-69, 4-1-70 ~~to~~ 10-31-70

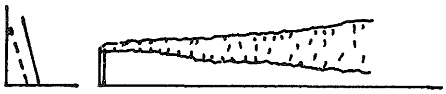
The manner in which stack effluents diffuse is primarily a function of the atmosphere. Church (1949) has typed the behavior of smoke plumes into five classes. Hewson (1960) had added a sixth class taking into account inversions aloft.

Looping



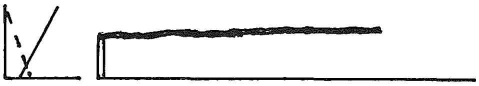
Looping occurs with a superadiabatic lapse rate. Large thermal eddies are developed in the unstable air and high concentrations may be brought to the ground for short time intervals. Diffusion is good however, when considering longer time periods. The superdiabatic conditions causing looping occurs only with light winds and strong solar heating. Cloudiness or high winds will prevent such unstable conditions from forming.

CONING



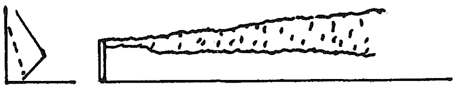
With vertical temperature gradient between dry adiabatic and isothermal, slight instability occurs with both horizontal and vertical mixing but not as intense as in the looping situation. The plume tends to be cone shaped hence the name. The plume reaches the ground at greater distances than with looping. Coning is prevalent on cloudy or windy days or nights. Diffusion equations are more successful in calculating concentrations for this type of plume than for any other.

FANNING



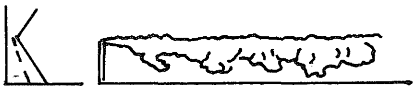
If the temperature increases upward the air is stable and vertical turbulance is suppressed. Horizontal mixing is not as great as in coning but still occurs. The plume will therefore, spread horizontally but little if any vertically. Since the winds are usually light the plume will also meander in the horizontal. Plume concentrations are high but little effluent from elevated sources reaches the ground with this situation except when the inversion is broken due to surface heating, or terrain at the elevation of the plume is encountered. Clear skies with light winds during the night are favorable conditions for fanning.

LOFTING



Lofting occurs when there is a superdiabatic layer above a surface inversion. Under this condition diffusion is rapid upward but downward diffusion does not penetrate the inversion and so is damped out. With these conditions gases will not reach the surface but particles with appreciable settling velocities will drop through the inversion. Near sunset on a clear evening in open country is most favorable for lofting. Lofting is generally a transition situation and as the inversion deepens is replaced by fanning.

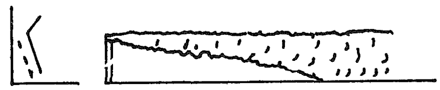
FUMIGATION



As solar heating increases the lower layers are heated and a superdiabatic lapse rate occurs through a deeper and deeper layer. When the layer is deep enough to reach the fanning plume, thermal turbulance will bring high concentrations to the ground along the full length of the plume. This is favored by clear skies and light winds and is apt to occur more frequently in summer due to increased heating.

Another type of fumigation may occur in the early evening over cities. Heat sources and mechanical turbulance due to surface roughness causes a lapse condition in the lower layers of the stable air moving into the city from non-urban areas where radiation inversions are already forming. This causes a fumigation until the city loses enough heat so that the lapse condition can no longer be maintained.

TRAPPING



When an inversion occurs aloft such as a frontal or subsidence inversion a plume released beneath the inversion will be trapped beneath it.

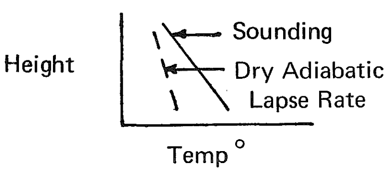


Figure 12. Influence of Vertical Temperature Variations on Stack Effluents[23]

APPENDIX XIII: SULFUR RECOVERY SYSTEMS

Presently there are at least fifty sulfur recovery methods under investigation or development. Emphasis is on processes which can clean up low concentration waste gases, while at the same time recover a marketable product of either sulfur or sulfuric acid. A third product, gypsum, is sometimes produced, however, since it is not normally marketable it is generally placed in storage.

There are two problems which a sulfur recovery system must be able to handle: (1) concentrations of SO_2 are usually quite low, and (2) the concentrations vary widely. Many of the smelting processes are batch processes. The SO_2 concentrations usually vary from 0% to 12% SO_2 or higher.

Following is a summary of some of the more promising sulfur recovery systems.

Limestone Injection

There are two types of limestone injection. In the first, pulverized limestone is injected into a furnace containing the offgases. Here it calcines and reacts in the gas phase to absorb sulfur oxides (dry process). In the second method, dry limestone is combined with wet scrubbing. The calcined limestone is removed by a scrubber and becomes the reactant which removes SO_2 from flue gases. This is one of the least expensive systems to operate, \$.015/million BTU; however, only 50% of the sulfur oxides can be removed. Several of the engineering problems include corrosion and scaling, potential water pollution, and waste disposal.

Alkalized Alumina

This process, which is being studied by the U.S. Bureau of Mines, is based on absorption of SO_2 from the effluent by $Na_2OA1_2O_3$. The absorbent is then regenerated by contact with reducing gases at high temperature and the resulting H_2S is converted to elemental sulfur in a standard Claus System. There are two major problems with this method. It is difficult to obtain a good contact between the absorbent solids and the flue gas, and small amounts of absorbent are lost during regeneration. This method will extract about 90% of the sulfur compounds from the effluent.

Catalytic Oxidation

In this process, SO_2 is converted to SO_3 by catalytic oxidation. The sulfur trioxide is then recovered without absorbent recycling and regeneration, and with very little cooling of the gas. Corrosion is the major problem with this type of system.

Electrolysis

In the electrolysis process, SO_2 is removed from the flue gas by reaction with caustic soda. This converts the caustic soda to sodium bisulfate which can then be stripped to release SO_2. The SO_2 is sent to a sulfuric acid plant and the remaining sodium sulfate solution is sent to an electrolytic cell. By use of a special membrane, the electrolytic cell can produce caustic soda, sodium acid sulfate, dilute sulfuric acid, oxygen, and hydrogen. The process claims to produce 99% sulfuric acid, while reducing the SO_2 of the stack gas to 50–150 ppm. Apparently, there are some operating problems with this procedure.

Catalytic Reduction

This process involves reaction of SO_2 in the stack gas with hydrogen sulfide over a catalyst to produce sulfur and water. Part of the sulfur is then recovered and the remainder reacts with methane to produce additional H_2S for use in the process.

Citrate Process

The U.S. Bureau of Mines has recently developed a citrate scrubbing method for recovering SO_2 from smelter gas, as elemental sulfur. The unit operations and flowsheet are shown in Figure 13 and are described as follows: Gas containing 1 to 3 percent SO_2 by volume is washed to remove particulate matter and SO_3. The gas is then passed upward through a packed absorption tower, countercurrent to a downward flow of a solution of citric acid ($C_6H_8O_7$) and Na_2CO_3. Over 90 percent of the SO_2 is absorbed by the citrate solution. The pregnant solution is reacted with H_2S in a stirred, closed vessel to precipitate the absorbed SO_2 as elemental sulfur. Scrubbing time in the reaction vessel is about 10 minutes at a temperature of about 50° C. The slurry of citrate solution and sulfur is thickened; the thickener underflow is centrifuged to recover stripped citrate solution for recycle with the thickener overflow to the absorption tower. The sulfur product is heated in an autoclave at 130°C and 35 psi to melt the sulfur and recover residual citrate solution for recycle. Two-thirds of the molten sulfur is then converted to H_2S for use in the sulfur precipitation reactor by vaporizing the sulfur and reacting the sulfur vapor with natural gas and steam in the presence of an alumina catalyst.

As a result of promising laboratory tests, a pilot plant was set up on a reverberatory furnace at the San Manuel smelter in Arizona. The pilot plant test confirmed the following laboratory findings.

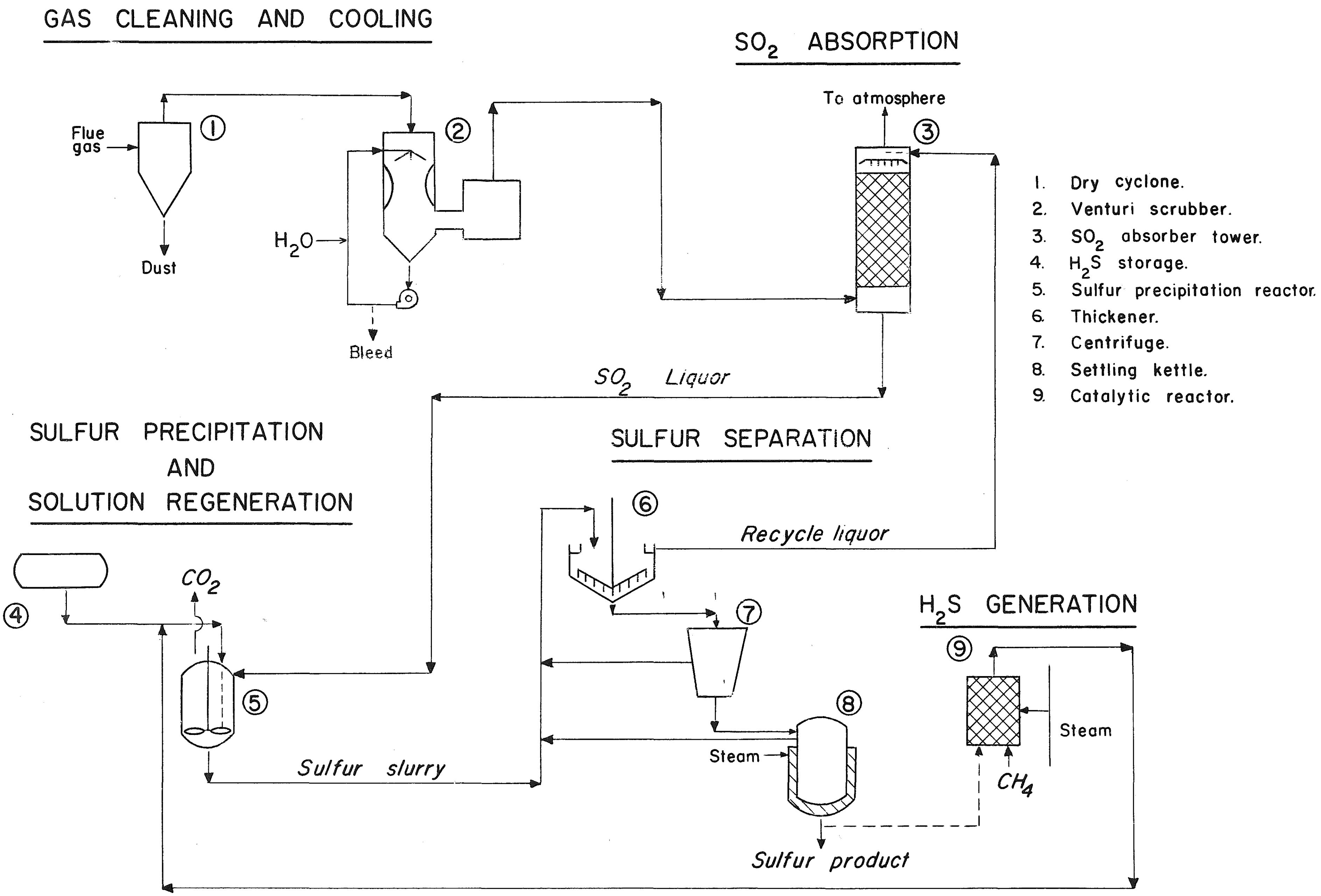


Figure 13. Generalized Citrate Process Flowsheet[23]

1. The citrate process will remove and recover 90 to 99 percent of the sulfur contained as SO_2 in copper reverberatory furnace flue gas.
2. Regeneration of solution and precipitation of sulfur with H_2S is readily controlled and highly efficient.
3. The precipitated sulfur can be continuously recovered as a high quality product by a combination of thickening, centrifuging, and melting.

Preliminary cost estimates are in the range of thirty-five dollars per ton of elemental sulfur recovered. If this could be sold for fifteen dollars per ton, then the net operating costs would be approximately twenty dollars per ton of recovered sulfur[8].

APPENDIX XIV: CURTAILED PRODUCTION

Many smelters are reducing or stopping production when concentrations of sulfur oxides are too high or during periods when the weather conditions do not allow good dispersion of the sulfur oxides. Two of the companies which follow this procedure are the Onahama Smelter and the United States Metals Refining Company.

Onahama Smelter

This facility, located in Japan, began operations in 1965 and is one of the most modern smelters in the world. The company maintains a smoke patrol, if more than 0.02 ppm SO_2 is detected, then the smelter must curtail operations. About twenty to twenty-five days of production are lost each year because of excessive sulfur oxide gas concentrations[24].

United States Metals Refining Company

This smelter, located at Carteret, New Jersey on Staten Island is a division of American Metal Climax, Inc. The company uses a semi-continuous automatic film monitoring system. When a film frame shows too much air pollution, that section of the operation is curtailed until the amount of pollution has been successfully reduced.

APPENDIX XV: PYROMETALLURGICAL EXTRACTION – ALTERNATE METHODS

Because of the air pollution problems associated with the conventional extraction methods, several alternate methods have been suggested as possible replacements. Such systems should attempt to incorporate the following features[25]:

1. Smelter systems must produce SO_2 in higher concentrations and in uniform volumes. This could probably be done by replacing batch processes with continuous processes and by combining extraction steps.
2. Gas cleaning systems must be more efficient and reliable and capable of operating at high temperatures.
3. Smelting operations must use less total fuel. More heat should be recovered and emphasis must be on heat utilization.
4. All useful materials should be recovered from the initial feed material. Waste products which are produced should be non-polluting and in a form which can be disposed of readily.

Four systems which are being considered to replace conventional methods are:

1. Continuous Smelting[26,27,28]
2. Flash Smelting[6,29,30]
3. Blast Furnace Smelting[6]
4. Electric Furnace Smelting[6]

Continuous Smelting

Two continuous smelting processes are being considered to replace conventional smelting. Noranda Mines Ltd. recently announced plans to build a $19 million commercial prototype of the Noranda continuous furnace shown in Figure 14. In Australia, the WORCRA process has been developed and the WORCRA continuous furnace is shown in Figure 15. Both methods combine conventional roasting, smelting, and converting steps into a single step. This results in higher concentrations of SO_2 that presumably can be recovered economically. The Noranda process is outlined as follows[27]:

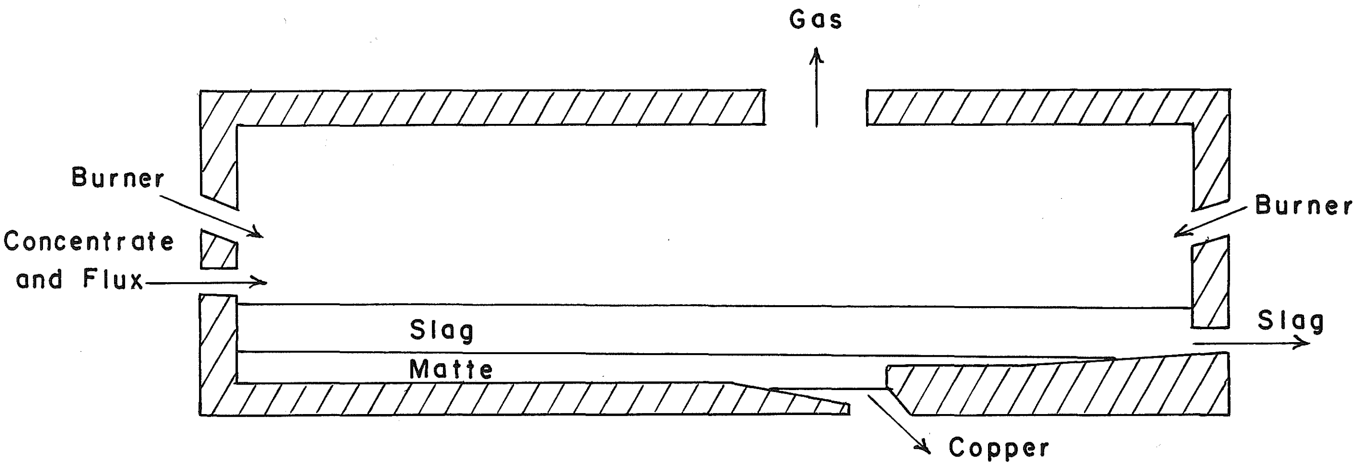


Figure 14. Noranda Continuous Smelting Furnace [27]

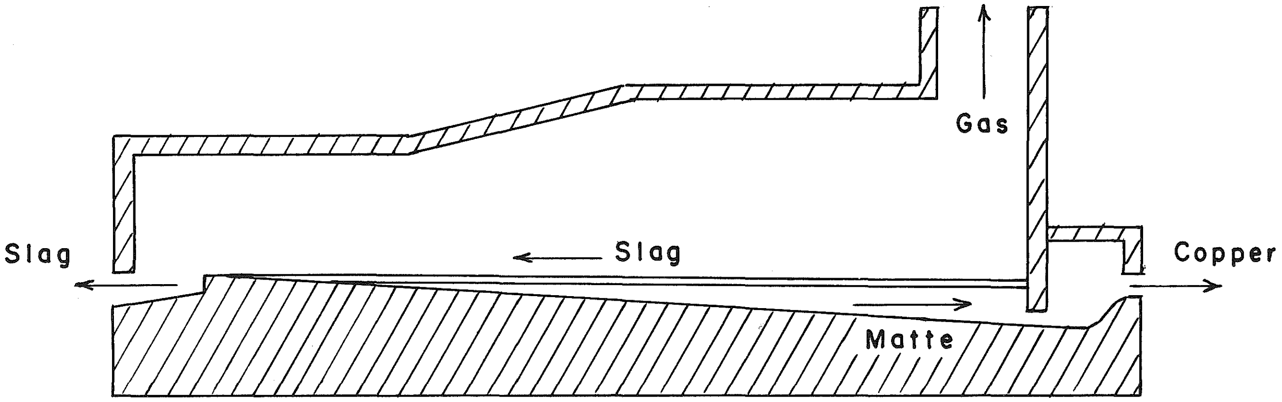


Figure 15. WORCRA Continuous Furnace [26]

1. *"Concentrates and feed are introduced in one end of the reactor which is similar in cross-section to a Pierce-Smith converter.*
2. *Smelting takes place at the feed end.*
3. *Matte and slag flows are controlled as they move slowly to tapping ports.*
4. *Oxidizing gas is introduced into the matte to oxidize the FeS.*
5. *Continued injection of the gas into the resulting white metal gradually oxidized the* Cu_2S *to metallic copper.*
6. *Metallic copper is tapped periodically after settling periods."*

The WORCRA process is outlined as follows[27]:

1. *"Metal is produced directly from concentrates in one unit.*
2. *Most of the exothermic oxidation reactions are generated and continue in the liquid bath.*
3. *Turbulence is generated in the smelting and converting zones by lance-injected oxygen-containing gas.*
4. *Slag moves countercurrent to matte and metal flow in the converting zone.*
5. *Copper-in-Slag is reduced to throw-away levels. There is no 'revert slag'.*
6. SO_2*-bearing gases of rich tenor exit through a single offtake. Furnace gases rich in* SO_2 *can be cooled and cleaned for waste heat utilization and production of sulfuric acid; or because of low oxygen content, the gases can be used to produce elemental sulfur."*

These processes have been successfully operated in pilot plants and commercial plants are under construction but as yet are untried on a commercial scale.

Flash Smelting

This process combines into a single operation, conventional roasting and smelting steps. The converting process remains the same as in traditional smelting. A sulfide concentrate is flash smelted by burning some of its sulfur and iron content while suspended in an oxidizing medium. The grade of the matte is controlled by regulating the ratio of oxygen to sulfur in the feed. Flash smelting combines two operations, and will hopefully permit economical treatment of flash furnace gases. The offgases from the converter are the same as those produced in conventional converting.

The flash smelter was developed after World War II and has been successfully operated in several commercial size plants using both copper and nickel concentrates as feed material. Figures 16 and 17 shows a cutaway view of two commercial flash smelters. Magma Copper Company recently announced plans to construct a flash smelter in Arizona as part of their pollution control program.

Blast Furnace Smelting

The blast furnace is a vertical shaft type furnace and may be used to produce either matte or blister copper. Matte is most commonly produced. Figure 18 shows a cutaway view of a blast furnace used to smelt nickel sulfide ore. As mentioned in Appendix V, the ore is mixed with the fuel and burned by blowing air through the mass.

This system combines roasting and reverberatory steps and occasionally when blister copper is produced, the converting step is also included. The main problem with blast furnace smelting is the excessive dust produced when air is blown through the mass. The ore must be either lump ore or sintered concentrates, with no fines present, if the furnace is to work effectively.

Electric Arc Furnace

Electric furnaces are sometimes used when electricity is cheap or when required smelting temperatures are very high. Figure 19 shows a cutaway view of a submerged arc electric furnace. Since there is no fuel combustion, the quantity of exit gas is greatly reduced. This produces higher SO_2 concentrations and easier heat and dust recovery. The electric furnace produces a matte, meaning the converter is still necessary to produce blister copper.

APPENDIX XVI: HYDROMETALLURGICAL EXTRACTION – RESEARCH

In the past, oxide leaching was the only hydrometallurgical method used for metal extraction from con-

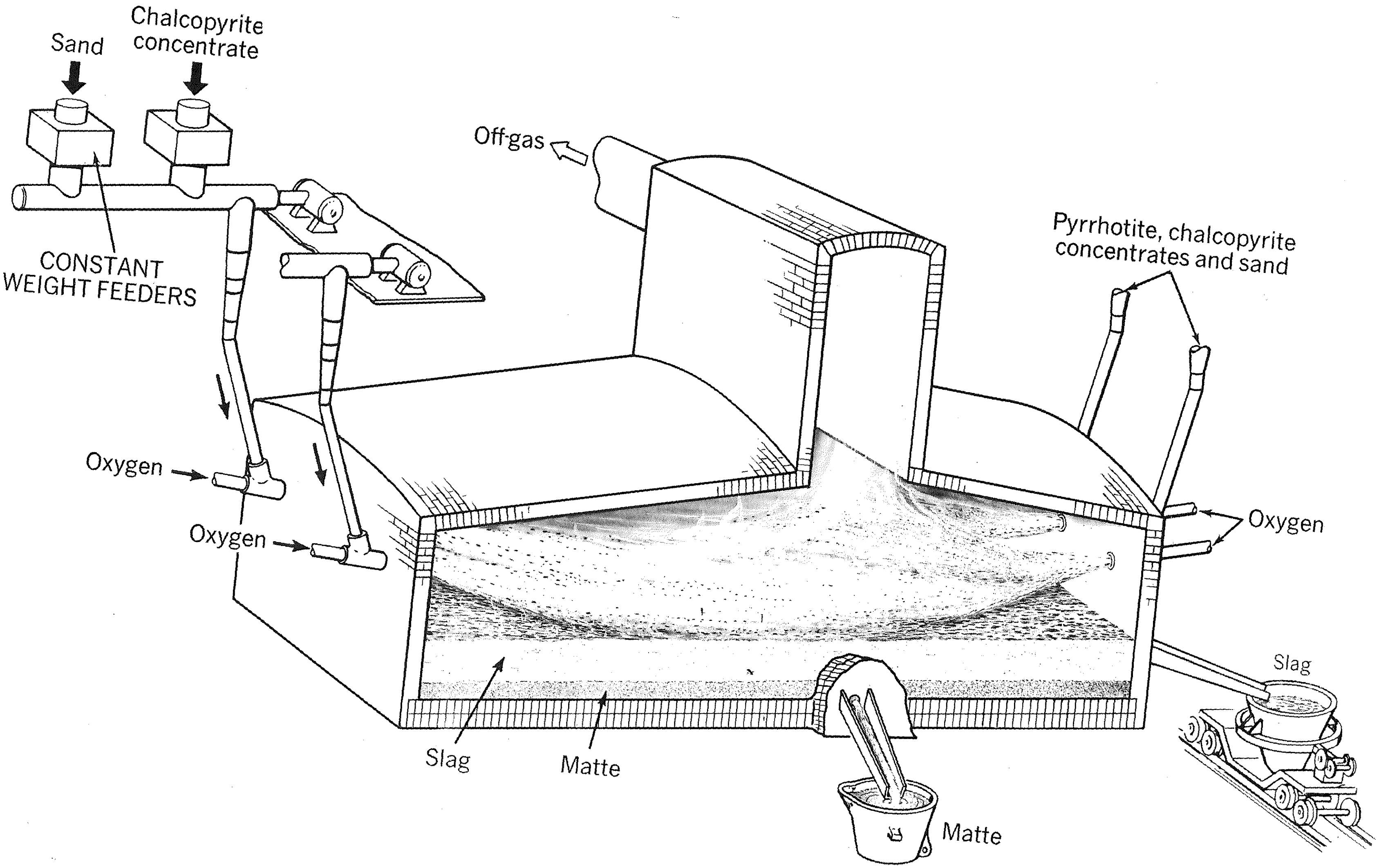


Figure 16 Cutaway View of INCO Oxygen Flash Smelting Furnace[6]

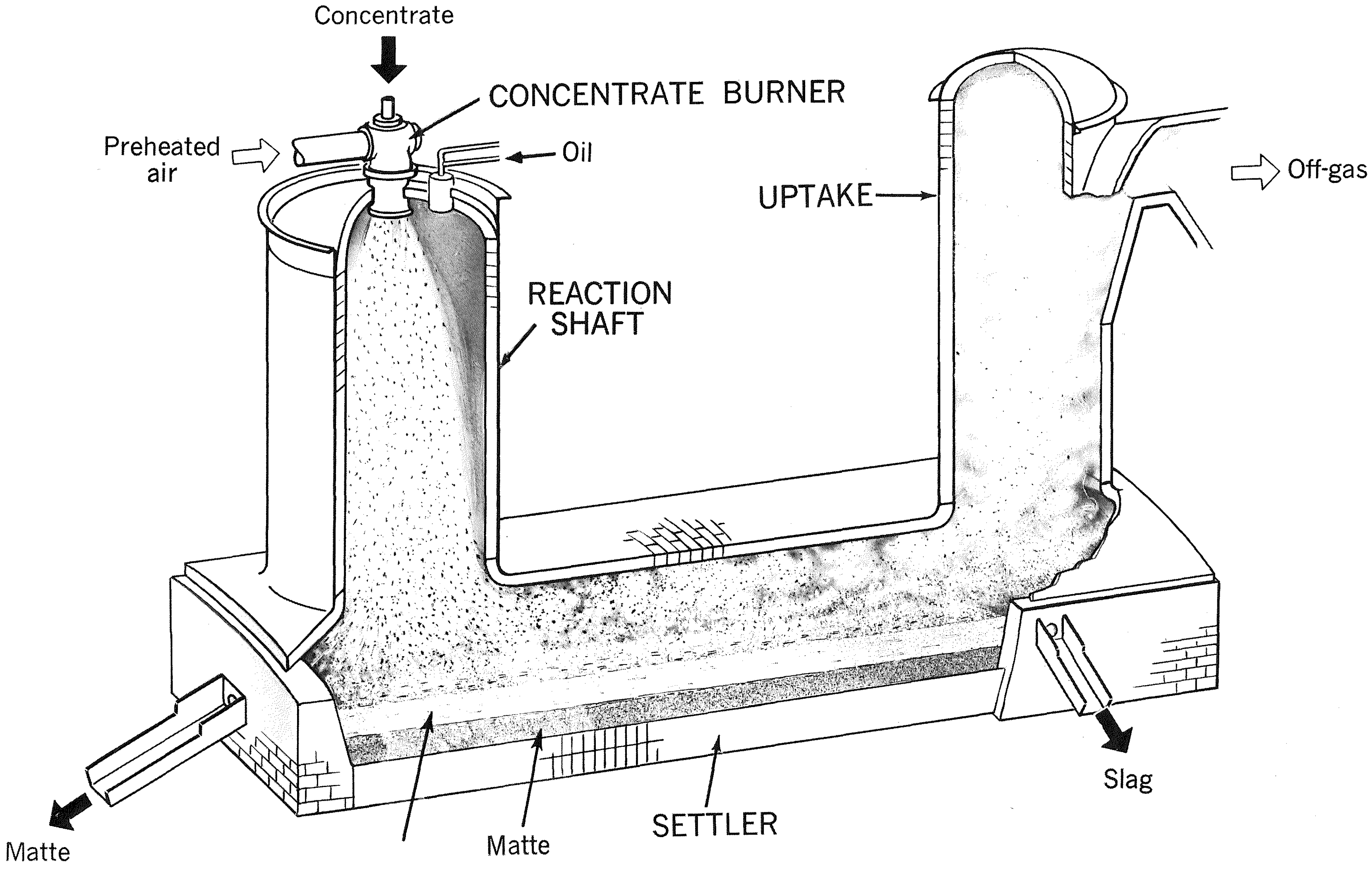


Figure 17 Cutaway View of Outokumpu Flash Smelting Furnace[6]

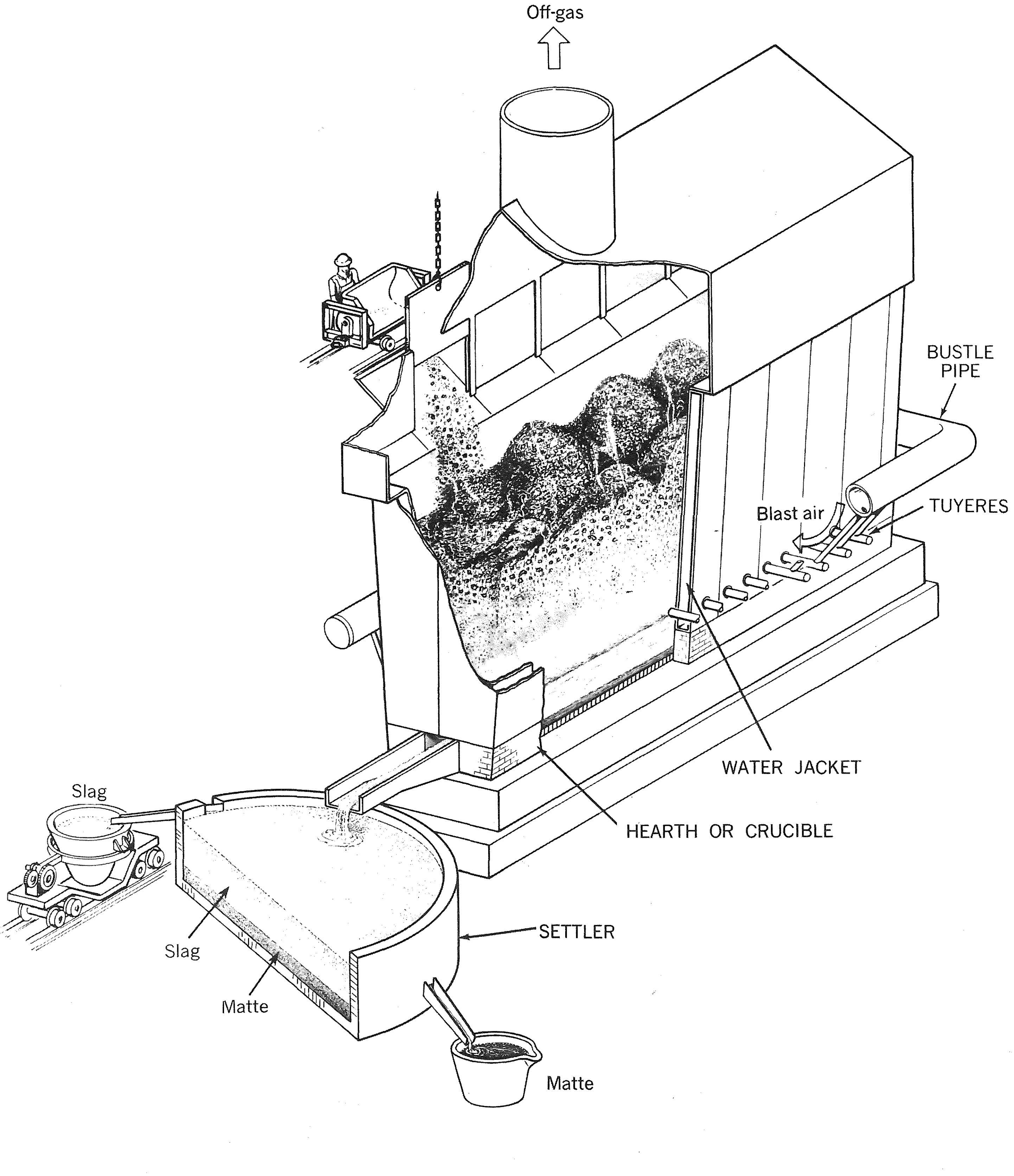


Figure 18 Cutaway View of a Blast Furnace for Sulfide Nickel Ore[6]

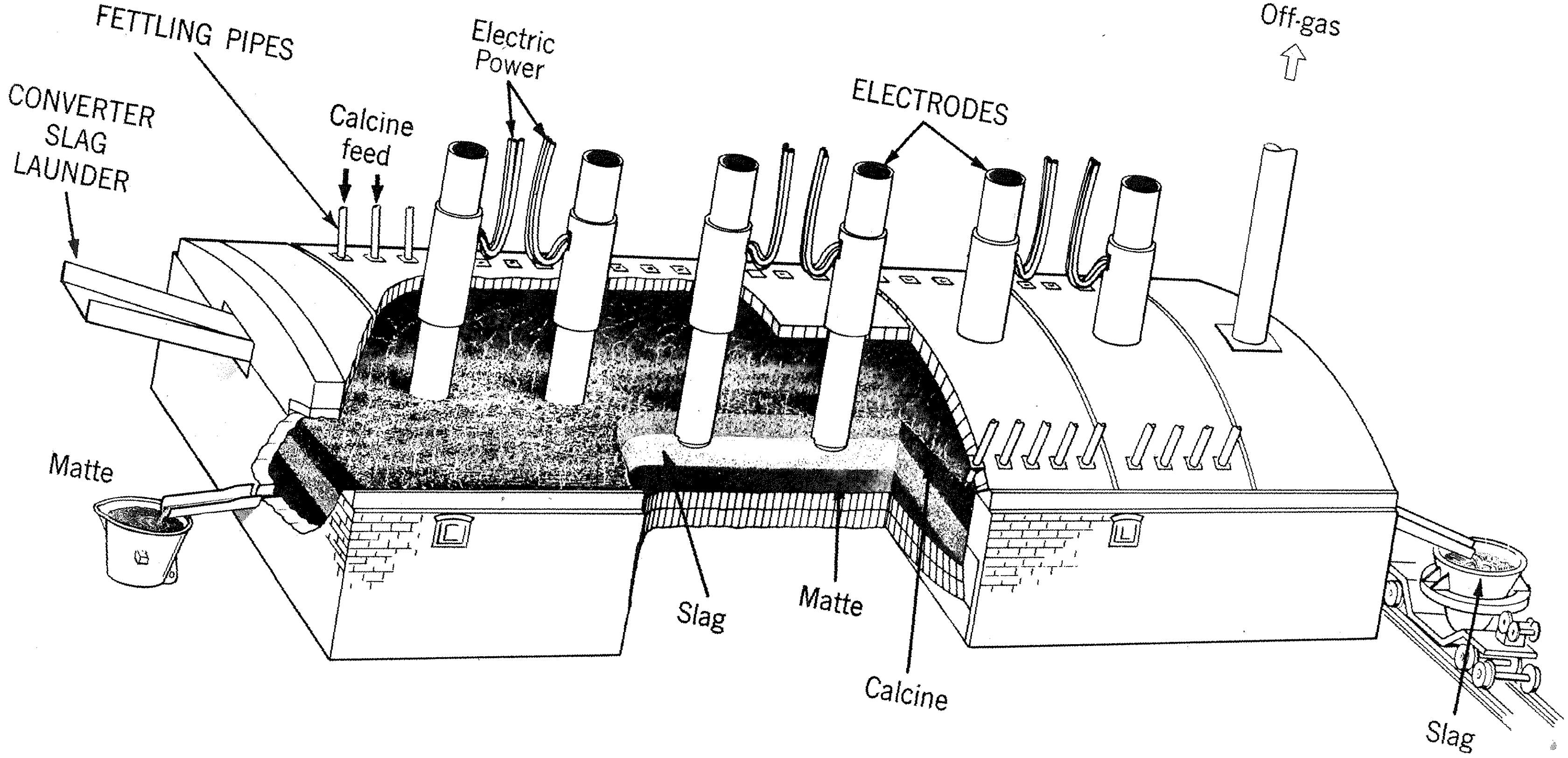


Figure 19 Cutaway View of a Submerged Arc Electric Furnace[6]

centrates. With increased emphasis on air pollution control, methods of leaching sulfide concentrates and rich sulfide ores directly (without prior roasting) are being studied. Most of these studies are in the laboratory stage of development, consequently metallurgical and economic data are not available.

Sherritt Gordon, Ltd., has developed a commercial process for treating nickel sulfides. However, it appears that Minnesota's deposits in the Gabbro contain primarily copper sulfides with small amounts of nickel so this process would not be applicable without modification. Two processes for treating copper sulfide ores are in the pilot plant stage. Short articles have been released by Duval Corporation and Anaconda Corporation announcing plans for these two plants. When considering the copper sulfide processes, it is important to remember that neither has been operated on a commercial scale.

Sherritt Gordon

Sheritt Gordon is operating a process which treats nickel sulfide ore, containing small amounts of copper[6]. The process is completely hydrometallurgical and final products consisting of nickel powder and copper sulfide concentrate (the copper concentrate must be smelted) are produced. If a high nickel ore body is found in Minnesota, this process would probably be considered.

More recently, Sherritt Gordon has joined with Cominco Ltd. to study a hydrometallurgical process that treats copper sulfides[31,32,33]. Progress on this project has not yet been reported.

Duval Corporation

In September, 1970, Duval announced the development of a hydrometallurgical process that treats copper sulfide concentrates. Concentrates are leached with a metal chloride solution, the metallic copper is separated, and the leaching solution is regenerated. To test the process, a pilot plant has been built at the Sierrita Mine, south of Tucson, Arizona.

The reactions involved are well known; however, it has never been possible to carry out the reactions under proper conditions or in a combination that will produce copper economically.

If the process proves economical, several advantages over the conventional pyrometallurgical process will be achieved. These include:

1. The process is continuous and takes place in a substantially closed system.
2. Sulfur dioxide gases will not be produced.
3. Electrolytic grade copper is produced, thus by-passing the refining operation.

If the pilot plant studies show the process to be economical, Duval, "in the interest of pollution", plans to license the process to industry "on a reasonable royalty basis"[34,35].

Anaconda Corporation

Anaconda Corporation has recently completed construction of a multimillion dollar pilot plant in Tucson, Arizona. The plant will test a hydrometallurgical process (Anatread Process) developed jointly by Treadwell Corporation and Anaconda Corporation. The process, if successful, will produce metallic copper directly from copper sulfide concentrates. This process will also produce elemental sulfur, a residual which can be easily treated for the recovery of associated minerals, and inert waste materials. The new process involves six steps. These include:

1. A sulfide concentrate is prepared by flotation.
2. The concentrates are then treated with strong sulfuric acid.
3. This solution is saturated with sulfur dioxide.
4. The saturated solution is reacted with 98% hydrogen cyanide, and copper is precipitated as cuprous cyanide (a white crystalline powder).
5. The powder is cleaned, dried, and briquetted.
6. At an elevated temperature of 400°C, hydrogen gas reduces the briquettes to metallic copper and hydrogen cyanide gas. The gas is recycled so that nothing is lost to the atmosphere.

The copper is electrolytic grade so that further refining is not necessary[36].

APPENDIX XVII: HYDROMETALLURGICAL EFFECTS AND CONTROL

Loss of Leaching Solution

Tank leaching is generally accomplished in a closed system, therefore, solution loss is not a problem. However, with in situ leaching or dump leaching, solution loss must be considered. Losses in dump leaching can be minimized or eliminated by depositing the ore on a waterproof pad. General steps for construction of such a pad were described in Appendix VI. Kennecott, in order to ensure minimal solution loss, drills and monitors wells near the site. Dump leaching is not a new technique. Methods are available that will minimize or eliminate water pollution. In situ leaching is only considered for highly fractured, extremely low grade ore bodies. Leaching solutions can be lost with this type of operation; however, it is unlikely that this method would be considered for Minnesota ores.

Disposal of Leaching Residuals

Water pollution problems that might be associated with the new hydrometallurgical processes mentioned in Appendix XVI are relatively unknown. Two possible problems can be considered.

In the Duval process, copper concentrates are leached with a metal chloride solution, the copper is removed, and the leaching solution regenerated. Water soluble chlorides may remain in the tailings. After tailings disposal, these could become a source of pollution.

A second problem could be the impurities that could dissolve in the leaching solution. Their disposal may also be a source of pollution.

The process Anaconda is testing, treats copper concentrates with sulfuric acid to produce a copper sulfate. The same two types of problems might also result - water soluble sulfates and disposal of leaching impurities.

APPENDIX XVIII: COMBINATION PYRO-METALLURGICAL – HYDROMETALLURGICAL EXTRACTION RESEARCH

Several systems are being evaluated that combine hydrometallurgy and pyrometallurgy to treat sulfide concentrates. Sherritt Gordon developed a sulphation roast process for treating nickel-cobalt ore that involves the following steps[37]:

1. Ore preparation includes size reduction and activation or blending to a suitable active feed.
2. The active feed is then mixed with concentrated sulfuric acid.
3. Roasting takes place under carefully controlled conditions.
4. The water soluble salts are leached at atmospheric pressures.
5. Precipitation of a mixed nickel-cobalt sulfur concentrate from the leach liquor is achieved with H_2S under pressure.

The concentrate must then be sent to a refinery for final purification.

The Bureau of Mines tried a somewhat similar method to extract copper and nickel from the Duluth Gabbro. The method used was a high temperature sulfatization process. *"Sulfatization is a process step in which an ore, concentrate, or plant byproduct is roasted in an atmosphere containing SO_3 and/or SO_2 and oxygen, slightly below the decomposition temperature of the sulfate salt of interest . . . Because the iron, copper, and nickel are present mainly as sulfides in the Gabbro, it is necessary that the sulfides be converted to oxides before sulfatization can occur. With excess air in the sulfatizing gas, this presents no problem."*[4] The sulfatization process converts the oxides to water soluble salts. These can then be leached in water. The results were as follows:

1. *"With a roasting temperature of 520°C, a roasting time of 3 hours, and a percent sulfur dioxide in the reaction gas between 13 and 26, over 95 percent of the copper can be sulfatized."*
2. *"Nickel sulfatization, however, is favored by a temperature of 670°C, a roasting time of five hours, and approximately 21 to 30 percent sulfur dioxide in the gas. With these conditions, over 80 percent of the nickel is sulfatized."*[4] The sulfatization must then be leached and reduced to elemental metal.

APPENDIX XIX: A CAPSULE VIEW OF U.S. COPPER SMELTING CAPABILITY[7]

	Charge Capacity	Roasters or Reactors	Reverberatory Furnaces		Converters	
			How Many	Dimensions (ft) (Width x Length)	How Many	Dimensions (ft) (Diameter x Length)
KENNECOTT						
Nevada Mines	400,000	–––	1	31 x 132	2	12 x 30
McGill, Nev.			1	32 x 132	1	13 x 30
					1 being installed	13.5 x 35
Chino Mines	400,000	–––	2	32 x 120	3	13 x 30
Hurley, N.M.					1 being installed	13 x 30
Ray Mines	420,000	Yes	1	35 x 120	3	13 x 30
Hayden, Ariz.						
Utah Copper	1,000,000	–––	3	38 x 123	9	13 x 30
Garfield, Utah						
ASARCO						
Tacoma, Wash.	600,000	Yes	1	22.25 x 112.75	3	13 x 30
			1	29.5 x 112.5	1	11 x 26
Hayden, Ariz.	960,000	Yes	1	30.5 x 115	3	13 x 30
			1	26.25 x 105	2	13 x 33
El Paso, Tex.	576,000	Yes	1	26.5 x 115.25	3	13 x 30
PHELPS DODGE						
Douglas Smelter	860,000	Yes	2	25.5 x 102.5	5	13 x 30
Douglas, Ariz.			1	27.25 x 103		
Morenci Branch	900,000	Yes	4	25.5 x 102.5	8	13 x 30
Morenci, Ariz.						
New Cornelia Branch	300,000	–––	1	30 x 100	2	13 x 30
Ajo, Ariz.						

APPENDIX XIX – Continued[7]

			Reverberatory Furnaces		Converters	
	Charge Capacity	Roasters or Reactors	How Many	Dimensions (ft) (Width x Length)	How Many	Dimensions (ft) (Diameter x Length)
ANACONDA						
Anaconda, Mont.	1,000,000	Yes	4	31 x 112	6	13 x 35
MAGMA						
San Manuel, Ariz.	403,000	–––	1 1 1	32 x 102 34 x 102 36 x 102	3 2	13 x 35 15 x 35
Superior, Ariz.	150,000	–––	Smelter scheduled to be shut down			
COPPER RANGE						
White Pine, Mich.	300,000	–––	2	NA	2	NA
INSPIRATION						
Miami, Ariz.	450,000	–––	1	30 x 120	1 3	12 x 20 13 x 23
CITIES SERVICE						
Copperhill, Tenn.	90,000	Yes	1	NA	1	NA

NA – Not Available

APPENDIX XX: CALCULATIONS OF NECESSARY RESERVES FOR THE VARIOUS EXTRACTION METHODS

Traditional Smelter

Minimum Smelter Size	1 Reverberatory Furnace 2–3 converters
Minimum Production Size	225 tons of blister copper per day[6,38] (97% pure)

Necessary Concentrate (25% Cu)

$$\frac{225\text{ tons/day} \times 0.97}{95\%\text{ smelter recovery }(0.25)} = 920\text{ tons/day}$$

Necessary Crude

1.5% crude $$\frac{920\text{ tons/day }(0.25)}{0.90\text{ recovery }(0.015)} = 17{,}000\text{ tons/day}$$

1.0% crude $$\frac{920\ (0.25)}{0.90\ (0.010)} = 25{,}500\text{ tons/day}$$

Necessary Reserves (25 yr. supply)

1.5% crude $25(365)\ (17{,}000) = 15.5 \times 10^7$ tons

1.0% crude $25(365)\ (25{,}500) = 23.3 \times 10^7$ tons

Flash Smelting

Minimum Size	1 Flash Furnace 2–3 converters
Minimum Production	230 tons of blister copper/day[30] (97% pure)

Necessary Concentrate (25% Cu)

$$\frac{230\text{ tons/day} \times 0.97\text{ pure}}{0.95\text{ recovery }(0.25)} = 940\text{ tons/day}$$

Necessary Crude

1.5% crude $$\frac{940\ (0.25)}{0.90\text{ recovery }(0.015)} = 17{,}400\text{ tons/day}$$

1.0% crude $$\frac{940\ (0.25)}{0.90\ (0.010)} = 26{,}000\text{ tons/day}$$

Necessary Reserves (25 yr. supply)

1.5% crude $25\ (365)\ (17{,}400) = 15.9 \times 10^7$ tons

1.0% crude $25\ (365)\ (26{,}000) = 23.7 \times 10^7$ tons

Continuous Smelting

Minimum Size	1 Continuous Smelting Furnace
Minimum Production	150 tons of blister copper/day[28,12]

Necessary Concentrate (25% Cu)

$$\frac{150\text{ tons/day} \times 0.97\text{ pure}}{0.95\text{ recovery }(0.25)} = 610\text{ tons/day}$$

Necessary Crude

1.5% crude $$\frac{610\ (0.25)}{0.90\ (0.015)} = 11{,}300\text{ tons/day}$$

1.0% crude $$\frac{610\ (0.25)}{0.90\ (0.010)} = 16{,}900\text{ tons/day}$$

Necessary Reserves (25 yr. supply)

1.5% crude $25(365)\ (11{,}300) = 10.3 \times 10^7$ tons

1.0% crude $25(365)\ (16{,}900) = 15.3 \times 10^7$ tons

Combination Roasting and Leaching

Minimum Size	1 Roaster
Minimum Production	100 tons of pure copper/day[6]

Necessary Concentrate (25% Cu)

$$\frac{100\text{ tons/day}}{0.25\ (0.95)} = 420\text{ tons/day}$$

Necessary Crude

1.5% crude $$\frac{420\ (0.25)}{0.90\ (0.015)} = 7{,}800\text{ tons/day}$$

1.0% crude $$\frac{420\ (0.25)}{0.90\ (0.010)} = 11{,}700\text{ tons/day}$$

Necessary Reserves (25 yr. supply)

1.5% crude $25(365)\ (7{,}800) = 7.1 \times 10^7$ tons

1.0% crude $25(365)\ (11{,}700) = 10.6 \times 10^7$ tons

Anatread and Duval Processes

Minimum Size	1 Leach Line (Fort Saskatchewan plant owned by Sherritt Gordon[6,32])

Minimum Production 50 tons of pure copper per day

Necessary Concentrate (25% Cu)

$$\frac{50 \text{ tons/day}}{0.25\ (0.95)} = 210 \text{ tons/day}$$

Necessary Crude

1.5% crude $\frac{210\ (0.25)}{0.90\ (0.015)} = 3{,}900$ tons/day

1.0% crude $\frac{210\ (0.25)}{0.90\ (0.010)} = 5{,}800$ tons/day

Necessary Reserves (25 yr. supply)

1.5% crude 25(365) (3,900) = 3.6×10^7 tons

1.0% crude 25(365) (5,800) = 5.3×10^7 tons

APPENDIX XXI: CALCULATIONS OF SULFUR RECOVERY COSTS WITH THE VARIOUS EXTRACTION PROCESSES

Traditional Smelting

Assumptions:

1. Crude ore contains 10% sulfur or 200 lbs/ton.
2. 50 lbs. of sulfur is removed during roasting. At 90% recovery, this yields 45 lbs of sulfur.
3. 50 lbs. of sulfur is removed in the reverberatory furnace. At 60% recovery, this yields 30 lbs. of sulfur.
4. 100 lbs. of sulfur is removed in the converter. At 90% recovery, this yields 90 lbs. of sulfur.
5. Net loss in roaster and converter recovery is \$28 – \$15 = \$13/long ton of sulfur.
6. Net loss in reverberatory recovery is \$35 – \$15 = \$20/long ton of sulfur.

Roasting: $\frac{233{,}000{,}000 \text{ tons} \times 45 \text{ lbs/ton} \times \$13}{2240 \text{ lbs/long ton}}$

Net Loss = \$60,850,000

Reverberatory: $\frac{233{,}000{,}000 \text{ tons} \times 30 \text{ lbs/ton} \times \$20}{2240 \text{ lbs/long ton}}$

Net Loss = \$62,410,000

Converter: $\frac{233{,}000{,}000 \text{ tons} \times 90 \text{ lbs/ton} \times \$13}{2240 \text{ lbs/long ton}}$

Net Loss: = \$121,700,000

Total Loss = \$244,960,000

Flash Smelting

Assumptions:

1. Crude ore contains 10% sulfur or 200 lbs/ton.
2. 100 lbs. of sulfur is removed during flash smelting. At 90% recovery, this yields 90 lbs. of sulfur.
3. 100 lbs. of sulfur is removed in the converter. At 90% recovery, this yields 90 lbs. of sulfur.
4. Net loss in extraction is \$28 – \$15 = \$13/long ton sulfur.

Extraction: $\frac{237{,}000{,}000 \times 180 \text{ lbs/ton} \times \$13}{2240 \text{ lbs/long ton}}$

Total Loss = \$247,600,000

Continuous Smelter

Assumptions:

1. Crude ore contains 10% sulfur or 200 lbs/ton.
2. All of the sulfur is removed during continuous smelting. At 90% recovery, this yields 180 lbs. of sulfur.
3. Net loss in continuous smelting is \$28 – \$15 = \$13/long ton sulfur.

Continuous Smelting: $\frac{153{,}000{,}000 \times 180 \text{ lbs/ton} \times \$13}{2240}$

Total Loss = \$159,800,000

Roasting as Part of a Combination System

Assumptions:

1. Crude ore contains 10% sulfur or 200 lbs/ton.
2. 100 lbs. of sulfur is removed during roasting. At 90% recovery, this yields 90 lbs. of sulfur.
3. Net loss in roasting is \$28 – \$15 = \$13/long ton sulfur.

Roasting: $\frac{106{,}000{,}000 \times 90 \times \$13}{2240}$

Total Loss = \$55,400,000

APPENDIX XXII: A REVIEW OF SEVERAL MINING COMPANIES' POLLUTION CONTROL PROGRAMS

As a result of governmental standards, companies are being forced to eliminate or reduce pollution caused by their operations. Following is a short list of companies and a summary of a portion of their pollution control programs.

Hudson Bay Mining and Smelting Co., Ltd.

This company plans to spend $2 million on research, in an effort to eliminate the discharge of sulfur dioxide gas into the atmosphere and to make the recovering of zinc more efficient. A pilot plant will be constructed having facilities for pressure leaching, purification, and electrolysis. If the results are favorable, the pressure leach method would be incorporated into the smelting process. Sulfur would be recovered as a by-product. This would decrease the amount of sulfur reaching the converter.

Kennecott Copper Corporation

The Ray Mines Division recently dedicated a silica ore leach plant at Ray, Arizona. The deposit has been known for a long time, but no method was available to treat the material (the deposit is not amenable to dump leaching). In conjunction, Kennecott built a $13 million sulfuric acid plant at nearby Hayden to provide the new leaching facility with the required sulfuric acid. The new plant at Hayden has the largest designed capacity of any plant using sulfur dioxide from two sources. The first is the fluosolids reactor, which roasts Cu concentrate, providing 14 to 16% SO_2. The second source is the converter furnace stack gases at a strength of 2 to 6% SO_2. This provides a strong enough concentration to allow the economic production of sulfuric acid.

International Nickel Co. of Canada, Ltd.

Plans are currently underway to build the largest metallurgical gas-based sulfuric acid plant in the world at Copper Cliff, Ontario. The plant will be built at an estimated cost of $20 million and a production capacity of 2,300 tons of sulfuric acid per day[39].

Tennessee Copper Company

The original practice here consisted of "heap roasting" followed by blast furnace and converter smelting. In the heap roasting procedure, trees were cut for fuel and the sulfur gas produced from roasting completed the destruction of the surrounding vegetation. A later development permitted direct smelting of the ore and elimination of the heap roasting step. However, Georgia farmers instigated a lawsuit which eventually reached U.S. Supreme Court. In 1907, a permanent injunction was granted severely limiting the discharge of sulfur dioxide. This led to the installation of chamber acid plants. The chief problem remaining to be solved is the reverberatory furnace stack gas, a problem which is common to all the copper smelters[40].

Cominco, Ltd.

Cominco recently announced that it would work jointly to develop a hydrometallurgical process for its Valley Copper Project in British Columbia. The process would be pressure leaching similar to that being used at Fort Saskatchewan.. It would treat copper concentrates, and produce as a by-product elemental sulfur[33].

Magma Copper Co.

In a plan recently presented to the Arizona Air Pollution Board, Magma Copper Co. plans to meet Arizona's emission standards by the end of 1973. They propose to do this by replacing one or more reverberatory furnaces in their San Manuel Smelter with one or two flash smelting furnaces. The facility will initially be designed to treat 710,000 tpy of copper concentrates and at the same time recover more than 90% of the contained sulfur[30].

American Smelting and Refining Company

In 1914, the Company organized a Department of Agricultural Research in Salt Lake City, Utah, to conduct research upon the effects of smelter gases on agricultural crops and methods of effluent control, particularly sulfur dioxide.

In 1928, they developed the Thomas Autometer, an instrument which could continuously detect, measure, and record minute quantities of the gas. The data collected from this instrument led ASARCO to the construction of tall smelter stacks when it was determined that high stacks more effectively dispersed gases into the atmosphere, where they are diluted and carried away.

Recently, ASARCO announced a $50 million program which would sharply reduce sulfur dioxide stack emissions from its copper smelters. A contract was recently awarded to Wellman-Power Gas, Inc. to design, engineer and construct a sulfuric acid system at its El Paso plant. The plant will produce 500 tpd of acid when it is completed.

FOOTNOTES

[1] Kingston, G.A., F.V. Carrillo, J.J. Gray, P. McLeroy, *Availability of U.S. Primary Nickel Resources,* Information Circular 8469, U.S. Bureau of Mines, 1970.

[2] Cochran W., Mine Subsidence, *Extent and Cost of Control in a Selected Area,* Information Circular 8507, U.S. Bureau of Mines, 1971.

[3] Grosh, W.A., J.W. Pennington, P.A. Wasson, & S.R.B. Cooke, *Investigation of Copper-Nickel Mineralization in Kawishiwi River Area, Lake County, Minnesota,* Report of Investigation 5177, U.S. Bureau of Mines, November, 1955.

[4] Joyce, Jr., F.E., *Extraction of Copper and Nickel From the Duluth Gabbro Complex by Selective High-Temperature Sulfatization,* Report of Investigation 7475, U.S. Bureau of Mines, January, 1971.

[5] LaBouurdais, DM, *Sudbury Basin,* Ryerson Press, Toronto, December, 1953.

[6] Boldt, Jr., J.R., *The Winning of Nickel,* D. Van Nostrand Company, Inc., Princeton, New Jersey, 1968.

[7] White, Lane, "SO_2 Laws Force U.S. Copper Smelters Into Industrial Russian Roulette", *Engineering and Mining Journal,* July, 1971.

[8] Rosenbaum, J.B., D.R. George, L. Crocker, W.I. Nissen, S.L. May, & H.R. Beard, *The Citrate Process for Removing SO_2 and Recovering Sulfur From Waste Gases,* U.S. Bureau of Mines, 1971.

[9] Sheffer, H.W. and L.G. Evans, *Copper Leaching Practices in the United States,* Information Circular 8341, U.S. Bureau of Mines, 1968.

[10] Evans, L.G. and H.W. Sheffer, "Dump and Heap Leaching Practices in the Western United States", *Mining Congress Journal,* September, 1968.

[11] Shoemaker, R.S. and R.M. Darrah, "The Economics of Heap Leaching", *Mining Engineering,* December, 1968.

[12] ____________ ,"Environmental Challenge: SO_2", *Engineering and Mining Journal*, April, 1971.

[13] McLeod, W. and R.R. Rogers, "Corrosion of Metals by Aqueous Solutions of the Atmospheric Pollutant Sulfurous Acid", *Electrochemical Technology,* July, 1969.

[14] ____________ , "Getting Sick of Sulfur in Tacoma", *The Wall Street Journal,* October 14, 1970.

[15] Barrett, T.W. and H.M. Benedict, "Sulfur Dioxide", *Recognition of Air Pollution Injury to Vegetation,* Air Pollution Control Association, Pennsylvania, 1970.

[16] ____________ , *Air Quality Criteria for Sulfur Oxides – Summary and Conclusions*, U.S. Department of Health, Education, and Welfare.

17 __________ , " Response of Guinea Pigs to SO_2 Gases", Air Pollution Control Association Journal, January, 1970.

18 Gross, Edward, The National Air Pollution Potential Forecast Program, Environmental Science Services Administration, Technical Memorandum WBTM NMC 47, Washington, D.C., May, 1970.

19 Graff, J.V., Supervisory Meteorologist and Principal Assistant, U.S. Department of Commerce, National Weather Service Forecast Office, Minneapolis/St. Paul, Minn., Personal Communication.

20 Strub, J.H., Jr., Meterologist in Charge, U.S. Department of Commerce, National Weather Service Forecast Office, Minneapolis/St. Paul, Minn., Personal Communication.

21 Crutcher, H.L. and D.K. Halligan, Upper Wind Statistics of the Northern Western Hemisphere, Technical Report, EDS-1, U.S. Department of Commerce.

22 Marsh, K.J. and M.D. Foster, "Experimental Study of the Dispersion of the Emissions from Chimney in Reading; Study of Long-term Average Concentrations of Sulfur Dioxide", Atmospheric Environment, September, 1967.

23 Turner, D.B., Pollution Concentration Variation.

24 Beall, J.V., "Onahama Smelter", Mining Engineering, May, 1969.

25 Argenbright, L.P., "Smelter Pollution Control", Mining Congress Journal, May, 1971.

26 __________ , "Smelting Metals Continuously", Engineering and Mining Journal, May, 1967.

27 __________ , "Two Direct Smelting Processes Designed for Pollution Control in Copper Plants", Engineering and Mining Journal, April, 1971.

28 __________ , "Noranda Pilots Continuous Copper Smelting", Engineering and Mining Journal, May, 1968.

29 Bridgstock, G., "How to Limit SO_2 Emissions With the Flash Smelting Process", Engineering and Mining Journal, April, 1971.

30 __________ , "Magma Copper Will Flash Smelt at San Manuel", Mining Engineering, June, 1971.

31 __________ , "Pollution-Free Copper Process Research", Skillings Mining Review, May 15, 1971.

32 __________ , "Sherritt Gordon Nickel's Unconventional Winner", Mining Engineering, October, 1968.

33 __________ , "Cominco – Sherritt Gordon Undertake Research on Pollution-Free Process", The Northern Miner, May, 1971.

34 ______________, "Duval Claims Development of 'Pollution-Free' Hydrometallurgical Copper Refining Process", *Engineering and Mining Journal*, September, 1970.

35 ______________, "Pollution-Free Process Found for Copper Recovery by Duval", *The Northern Miner*, December 31, 1970.

36 ______________, "Anaconda On the Brink of a Metallurgical Break-through", *Mining Engineering*, June, 1971.

37 ______________, "All Eyes Are Now on Nickel Hydrometallurgy", *Engineering and Mining Journal*, October, 1968.

38 ______________, "Copper in Andes", *Mining Engineering*, November, 1969.

39 ______________, "Inco's New Smelter", *Engineering and Mining Journal*, September, 1969.

40 Jones, E.M., "Air and Water Pollution Control at Tennessee Copper Co.", *Mining Congress Journal*, October, 1968.

BIBLIOGRAPHY

1. ____________ , Air Pollution Control, Rules, Regulations, and Air Quality Standards, Minnesota Pollution Control Agency, 1969 Edition.

2. ____________ , "Air Quality and American Smelting and Refining Co.", Min. Congress Journal, November, 1968.

3. Andrews, R.W., Jr., "Controlling Pollution in Aluminum Smelting", Metal Progress, May, 1969.

4. Baker, D.G. and Strub, J.H., Jr., "Climate of Minnesota, Part III Temperature and Its Application", Univ. of Minnesota Technical Bulletin 248, 1965.

5. Baker, D.G., Haines, D.A., and Strub, J.H., Jr., "Climate of Minnesota, Part V. Precipitation Facts, Normals, and Extremes", Univ. of Minnesota Technical Bulletin 254, 1967.

6. Barrett, T.W. and H.M. Benedict, "Sulfur Dioxide", Recognition of Air Pollution Injury to Vegetation, Air Pollution Control Association, Pittsburgh, Pennsylvania, 1970.

7. Beals, G.C. and J.J. Cadle, "Copper and By-Product Sulfuric Acid Production by Palabora Mining Co.", Journal of Metals, July, 1968.

8. Beamish, J. and H. Harvey, "Why Trout are Disappearing in LaCloche Lakes", The Globe and Mail, July 26, 1971.

9. Bell, D.H., "Smokeless Smelter is Aim of Industry", The Northern Miner, April 29, 1971.

10. Boyer, A.E. and F.B. Kaylor, "Can the Cost of SO_2 Pollution Control be Reduced?" Power, April, 1969.

11. Chamberlain, "How Cyanidation Can Treat Copper Ores", Engineering and Mining Journal, October, 1969.

12. Connor, J.M., "Economics of Sulfuric Acid Manufacture", Chemical Engineering Progress, November, 1968.

13. Coons, J.D., "Plume Visibility As a Control Basis", Mining Congress Journal, April, 1968.

14. ____________ , "Copper Refinery: U.S. Metals Refinery Co.", Air Pollution Control Association Journal, October, 1967.

15. Dayton, "Treasury Readies a New Time Bomb", Engineering and Mining Journal, July, 1971.

16. Farkas, M.D. and R.R. Dukes, "Multiple Routes to Sulfuric Acid", Chemical Engineering Progress, November, 1968.

17. Fletcher, A.W. and K.D. Hester, "A New Approach to Copper-Nickel Ore Processing", A.I.M.E. Transactions, September, 1964.

18. Freyman, J. and G.T. Armstrong, A Cost-Benefit Analysis on the Feasibility of Establishing a Lead-Zinc Smelter in the Northwest Territories of Canada, Department of Indian Affairs and Northern Development, Ottawa.

19. George, D.R., et al, "The Recovery of Elemental Sulfur From Base Metal Smelters", Mining Engineering, January, 1970.

20. Gilliland, J.C., "Water Pollution Control and the Minerals Industry", Mining Congress Journal, April, 1968.

21. Gorham, E., "Pneumonia and Atmospheric Sulphate Deposit", The Lancet, September 5, 1959.

22. Gorham, E. and A.G. Gordon, "Some Effects of Smelter Pollution Northeast of Falconbridge, Ontario", Canadian Journal of Botany, 1960.

23. Guccione, "The War on Pollution is Being Won", Engineering and Mining Journal, July, 1971.

24. Habashi, "Processes For Sulfur Recovery From Ores", Mining Congress Journal, June, 1969.

25. Hass, L.A., T.A. McCormick, and S.E. Khalafalla, Removing Sulfur Dioxide by Carbon Monoxide Reduction, Report of Investigation 7483, U.S. Bureau of Mines, March, 1971.

26. Haver, F.P. and M.M. Wong, Recovering Elemental Sulfur From Nonferrous Minerals, Report of Investigation 7474, U.S. Bureau of Mines, January, 1971.

27. Hendowi, I.J., "Injury by Sulfur Dioxide", Air Pollution Control Association Journal, 18:307-12 May, 1968.

28. High, M.D. and W.H. Megonnell, "Pollution Control", Mechanical Engineering, February, 1969.

29. Hochheiser, S., F.J. Burmann, and G.B. Morgan, "Atmospheric Surveillance – The Current State of Air Monitoring Technology", Environmental Science and Technology, August, 1971.

30. Jones, J.R., "Air Pollution – Impact of Legislation", Mining Congress Journal, April, 1968.

31. Kissander, A.R., Jr., A Bit of Smokestack Meteorology, University of Arizona.

32. Kronseder, J.G., "Cost of Reducing Sulfur Dioxide Emissions", Chem. Eng. Prog., November, 1968.

33. Mahoney, P.G. and F.W. Starratt, "Revamping Largest Copper Smelter in the U.S.", Engineering and Mining Journal, April, 1968.

34. McGarr, H.J., N.H. Berlin, W.F.A. Stolk, "The Cost of Copper Solvent Extraction and Electrowinning Look Great on Paper", Engineering and Mining Journal, December, 1969.

35. McMahon, A.D., Copper – A Materials Survey, Information Circular 8225, U.S. Bureau of Mines, 1965.

36. Medding, B. and D.J.I. Evans, "The Changing Role of Hydrometallurgy", The Canadian Mining and Metallurgical Bulletin, February, 1971.

37. ______________, "Monkey and Guinea Pigs Sub for Humans in SO_2 Tests", Electrical World, December 8, 1969.

38. Neiburger, M., "Meteorological Aspects of Air Pollution Control," Yale Scientific Magazine, January, 1967.

39. ________________, "New Sherritt Gordon Process Treats Sulphide and Oxide Nickel Ores", *Engineering and Mining Journal*, September, 1969.

40. Pirsch, E.A., "New Approach Offers Economic SO_2 Control Method", *Electrical World*, November 18, 1968.

41. ________________, "Pollution Control – And Byproduct Sulphur, Too, Part II", *Engineering and Mining Journal*, June, 1968.

42. Ramarez, P., "New Criteria Prod. Search for SO_2 Control Method", *Chemical Engineering*, October 21, 1968.

43. ____________, "Response of Guinea Pigs to SO_2 Gases", *Air Pollution Control Association Journal*, January, 1970.

44. Schenck, G.H.K. and H.W. Robinson, "Who Needs a Private Weather Service", *Mining Engineering*, April, 1971.

45. Shah, I.D. and S.E. Khalafalla, *Chemical Reactions in the Roasting of Copper Sulfides*, Report of Investigation 7459, U.S. Bureau of Mines, December, 1970.

46. ________________, "Smelters Poised for Move Into Sulfur: Special Report on Sulfur From Ore", *Canadian Chemical Process*, March, 1968.

47. Snow, R.H., *Proposal for Group-Sponsored Research Project on Pollution- Free Copper Extraction*, IIT Research Institute, Chicago, Illinois, June, 1970.

48. Stites, J.G., "Successful Removal of Sulfur Dioxide From Flue Gas", *Mining Congress Journal*, June, 1969.

49. ____________, "SO_2, Is it a Health Hazard Under Normal Conditions?" *Coal Age*, April, 1968.

50. ____________, "Sulfur Dioxide, a Harmless Pollutant?", *Production Engineering*, February 26, 1968.

51. Sullivan, G.D., "Mining Industry and Environmental Control", *Mining Congress Journal*, February, 1968.

52. ________________, "Sulphur: The Economics of New Recovery Systems, Part I", *Engineering and Mining Journal*, May, 1968.

53. Swan, D., "Study of Costs for Complying With Standards for Control of Sulfur Oxide Emissions From Smelters", *Mining Congress Journal*, April, 1971.

54. ________________, "Tax Incentives for Clean Industries", *Environmental Science and Technology*, August, 1971.

55. Thompson, R. and E.B. Butler, "History of Sulfuric Acid Production from Converter Gas at the Kennecott Copper Corp's Utah Smelter", *Journal of Metals*, July, 1968.

56. ________________, *TOPSOE/SNPA Sulfuric Acid Process for the Recovery of Sulfur and Sulfur Compounds from Dilute Roaster Gas*, Haldor Topsoe, Inc., New York, New York.

57. Town, J.W., J.H. Russell, and H.J. Kelley, Removing Sulfur Dioxide From Flue Gases, Report of Investigation 7478, U.S. Bureau of Mines, February, 1971.

58. ________________________, "Trends in Copper Hydrometallurgy", Chemical and Process Engineering, January, 1970.

59. ______________, World's Largest Chimney, M.W. Kellogg Company, Williamsport, Pa., 1971.

60. Wornes, H.K., "WORCRA Metallurgy Looks Promising for Pollution Control in Copper Plants", Engineering and Mining Journal, August, 1971.