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AIR POLLUTANT
EMISSION FACTORS

Supplement

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Environmental Health Service
National Air Pollution Control Administration

TRW
SYSTEMS GROUP OF TRW INC.

This report presents emission factors for five industrial processes that were not covered in earlier studies. It supplements the April 1970 report on Air Pollution Emission Factors, and was likewise compiled by Resources Research, Inc., TRW Systems Group for the National Air Pollution Control Administration, Division of Air Quality and Emission Data, under Contract No. CPA 22-69-119.

TABLE OF CONTENTS

COAL PREPARATION

Coal as mined, called "run-of-mine" or "through" coal, is usually a mixture of sizes from lumps 3 feet long to the finest dust. It also includes "dirt" or "shale" (not to be confused with rock of the same name), which may vary from pure stony matter to carbonaceous mixtures. Coal is brought to the surface in tubs or skips and tippled on to shaking screens which separate the large coal from the small coal. The nature of these operations varies with the character of the coal. If it is hard and free from shale partings, the simple screening into large and nut sizes and smaller slack and "duff" may be all that is required for marketability. The large coal is usually hand picked and individually cleaned of shale remnants. When coal is friable and there is much small and when it is dirty due to intermixture of shale, cleaning by washing and more elaborate sizing become necessary.

Most cleaning is done by a wet process, using water or a "dense medium" of finely ground magnetites or barytes in colloidal suspension in water. The operation of every mechanical coal-cleaning process depends on the difference in specific gravity of the four ingredients: water, with specific gravity of 1, coal about 1.35, shale about 2.3, and iron pyrites about 5.0. Cleaning is done by washing in either continuous current or pulsating (jigging) machines, where the lighter coal near the surface is removed by a stream of water while the heavier waste falls and is discharged at a lower level or at the bottom of the machine. Two devices are shown in Figures 1 and 2 (Ref. 1).

A dry "washing" or cleaning process is also in use, particularly for cleaning nut coal, where the use of water would cause discoloration of the coal and lessen its marketability. The coal passes over an inclined glass plate which is kept clean by a stream of compressed air. In another dry cleaning device, the coal is passed over a shaking table with a perforated deck through which a current of air blow upward. In each case the shale, being heavier, sinks to a lower level and through a gap, while the coal passes on. Dry cleaners are not as efficient as

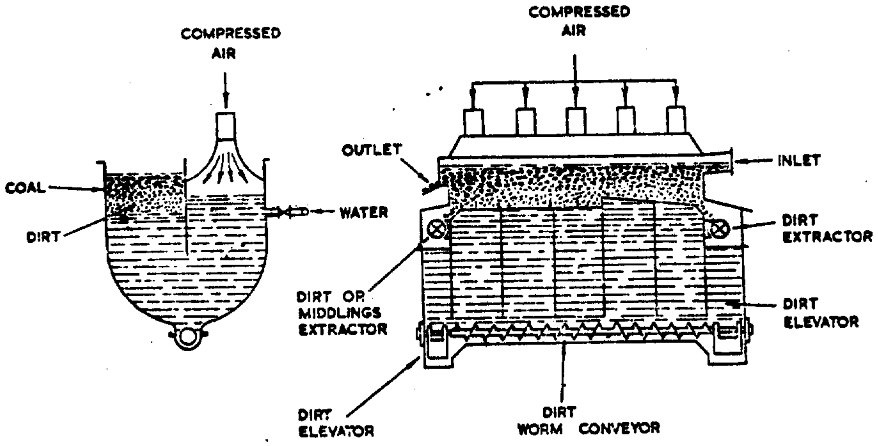


Figure 1. The Baum Coal Washer

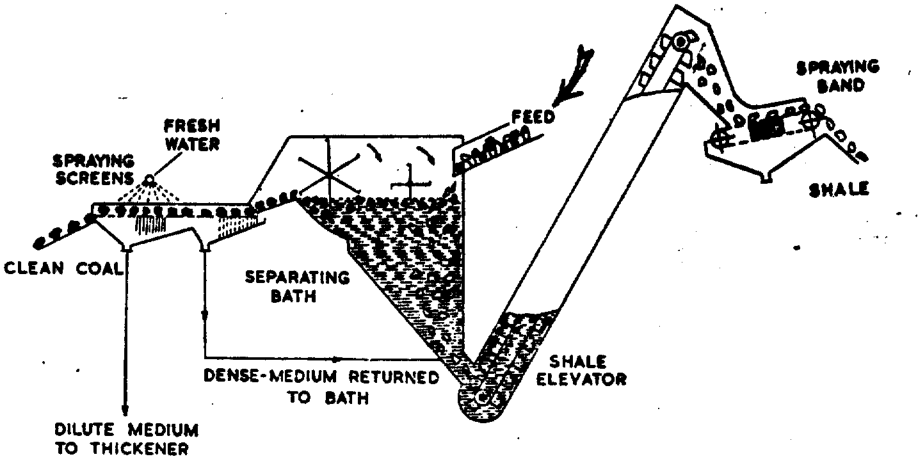


Figure 2. Dense Medium Coal Cleaner

wet washers, and their use is dying out rapidly since water is often used underground to scrub coal dust as a prevention against dust diseases (e.g., pneumoconiosis), and the coal is brought up too wet to be cleaned by dry methods.

Particulate matter that separates from the coal during transport, screening, and entry into the cleaner may cause air in the immediate vicinity of the equipment to be dusty; but otherwise coal preparation up to the drying stage is generally free of emissions to the ambient atmosphere. The major source of air pollution is the exhaust from thermal coal dryers.

Seven types of thermal dryers are presently used:

Rotary. There are two kinds; double shell indirect heated and outer shell only with lifting vanes inside. (See Figure 3, Ref. 2.)

Screen. Moisture is evaporated by hot gases passing through coal conveyed on a reciprocating screen.

Cascade. Coal is dried by flowing through a series of stationary or revolving shelves.

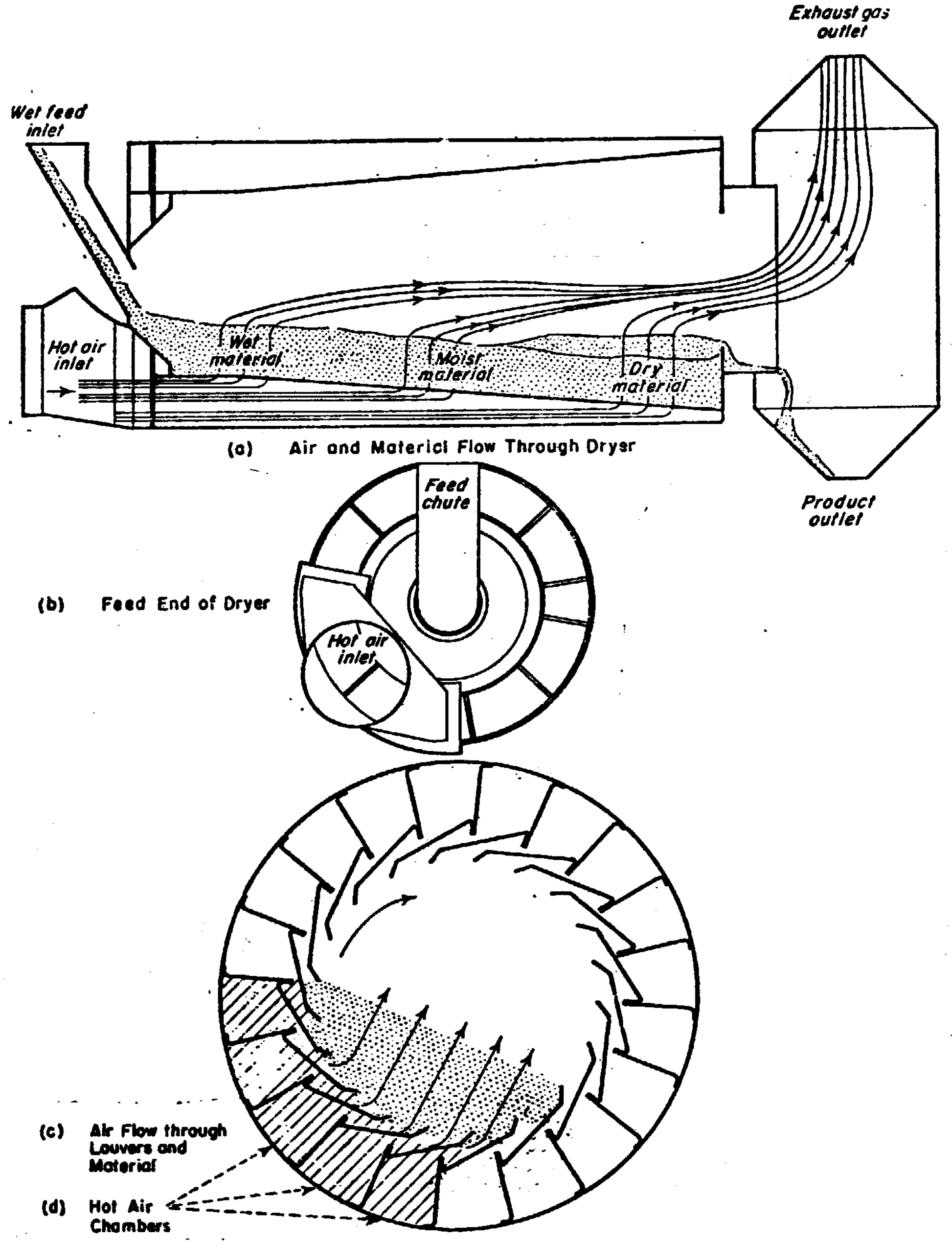
Continuous Carrier. Coal is moved through the dryer on a wire mesh belt.

Flash or Suspension. Coal is fed into a stream of hot gases where instantaneous drying occurs. The dried coal and wet gases are drawn up a drying column and into the cyclone for separation.

Multilouver. Hot gases are passed through falling curtains of coal. The coal is raised by flights of a specially designed conveyor.

Fluidized Bed. The coal is suspended and dried in a fluid state above a perforated plate by rising hot gases. (See Figure 4, Ref. 2.)

The fluidized bed type has been the most popular in recent years. The gas volumes from this type of dryer range from 50,000 to 250,000 acfm. The exit gas temperature will be about 200°F. Dust concentrations in



(a) Air and Material Flow Through Dryer

(b) Feed End of Dryer

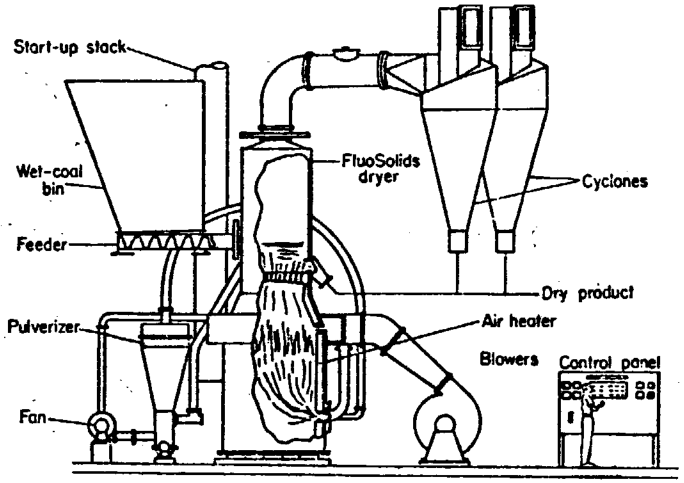
(c) Air Flow through Louvers and Material

(d) Hot Air Chambers

Figure 3. Link-Belt Roto-Louvre Dryer (Link-Belt Co.)

Figure 4. Fluidized-bed Coal Dryer

(courtesy of Dorr-Oliver, Inc.)



the gases from the dryer are unusually high - 100 to 300 grains per actual cubic foot (gr/acf). A typical particle size analysis of feed to the fluidized bed dryer is listed in Table I.

It is assumed that all the minus 200 mesh material is carried to the cyclones. This means as much as 35% to 40% of the total feed to the dryer is carried over to the primary collectors.[3] No dryers are operated without collectors, and the exhaust gas is fully contained until it leaves the collector system. Hence, the emission data presented here apply to the exhaust gas after control.

Table I Typical Particle Size Analysis of Feed to a Fluidized Bed Dryer[1]

Particle size, microns	% by Weight less than State Size
500 (32 mesh)	98%
300	90%
200	78%
100	43%
75 (approximate 200 mesh)	28%
40	7%
20	1%

Table II is a listing of typical particle size analyses of material vented from several types of dryers to primary collectors.

Table II Typical Particle Size Analyses of Material to the Cyclones[3]

	% by Weight less than Stated Size		
Particle Size, microns	Flash Dryer*	Fluidized Bed	Cascade & Multilouvered
60	98	20	70
40	96	14	50
20	90	5	42
10	80	2	25
5	65	0.5	10
2	40	0.1	2.5

NOTE: The average dust concentration from each dryer type:

Flash - 2 gr/acf
Cascade and Multilouvered - 20 gr/acf
Fluidized Bed - 200 gr/acf

*Outlet from main cyclone

EMISSIONS

West Virginia, which is the largest coal producing state in the Union, has adopted Regulation V for the control of thermal coal dryers. The maximum allowable emission, for a dryer exhausting 110,000 cfm or less, is 0.10 grains per standard cubic foot (gr/scf). After September 1, 1971, the limit will be 0.09 gr/scf.

However, it has been reported that to obtain a "clear stack" (no visible emission of coal dust fines) the particulate concentration must be below 0.038 gr/scf.[3]

In one case, a particulate grain loading of 0.047 gr/scf, in the effluent gases from a thermal coal dryer stack, produced an evident gray coal dust plume.[4] After installation of a venturi scrubber system, the outlet grain loading of 0.023 gr/scf produced a plume with no visible emission of coal dust fines. For the particular unit which was tested, the first grain loading corresponded to an emission rate of 38 lbs/hour and the second concentration corresponded to a rate of 15 lbs/hour. The concentration, quantity and particle size range of emissions depend upon the type of collection equipment used to reduce particulate emissions from the dryer stack. Some typical grain loadings from various control equipment are:

Type of Control	Outlet Grain Loading, gr/scf
Cyclones (product recovery)	6-9 gr/scf
Multiple cyclones (product recovery)	2.5-3.5 gr/scf
Water Sprays*	0.7-1.5 gr/scf
Wet scrubber*(pressure drop less than 5 inches H_2O)	0.1-0.2 gr/scf
Wet scrubber*(pressure drop 8-15 inches H_2O)	0.035-0.05 gr/scf
Wet scrubber*(pressure drop greater than 20 inches H_2O)	0.02-0.03 gr/scf

*Following product recovery systems on the thermal dryer effluent.

Collection efficiencies over 99% are achievable by use of a scrubber on a fluidized bed cyclone,[3] as shown by Figure 5. Greater collection efficiency can be obtained by using cyclones with a fluidized bed dryer than with certain other types of dryers,[3] for the same pressure drop. See Figure 6.

Practically, to meet the present regulations and public demands, wet scrubbers must be employed to control the emissions from thermal coal dryers. With wet scrubbers, the outlet grain loading is inversely related to the energy expended in the scrubber, which is measured by the scrubber pressure drop. Simply, the greater the pressure drop, the greater the collection efficiency.

Table III lists recommended emission factors for the only dryers to which any data were available . (See Appendix.) These figures are tenuous because of the scarcity of published data.

Table III Emission Factors for Thermal Coal Dryer:
Pounds of Particulate per ton of Coal Dried(after control)

Type of Thermal Dryer	Particulate Emission from Product Recovery System
Fluidized Bed	6
Flash	5
Multilouvered	7.5

FACTORS AFFECTING EMISSIONS

Dust emissions are not related to the percentage of fines nor to the moisture in the dryer feed or product. Increasing the amount of coal filter coke in the feed also has no effect upon emissions. However, emission control from a thermal coal dryer hinges upon the selection of an adequate collection device and proper use of this equipment. In the case of scrubbers, for example, if a venturi system is used, the pressure drop must be regulated and maintained. With impingement scrubbers the prescribed critical speed for impingement must be maintained.

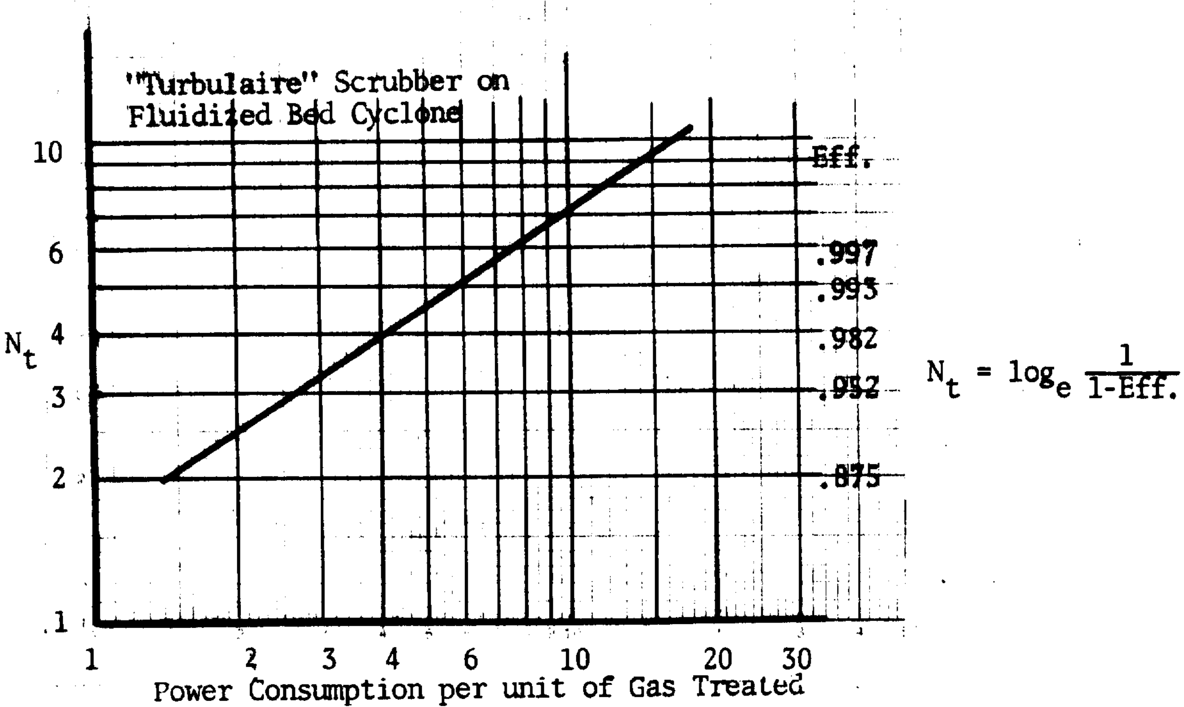


Figure 5. Relation between Power Consumption and Scrubber Efficiency

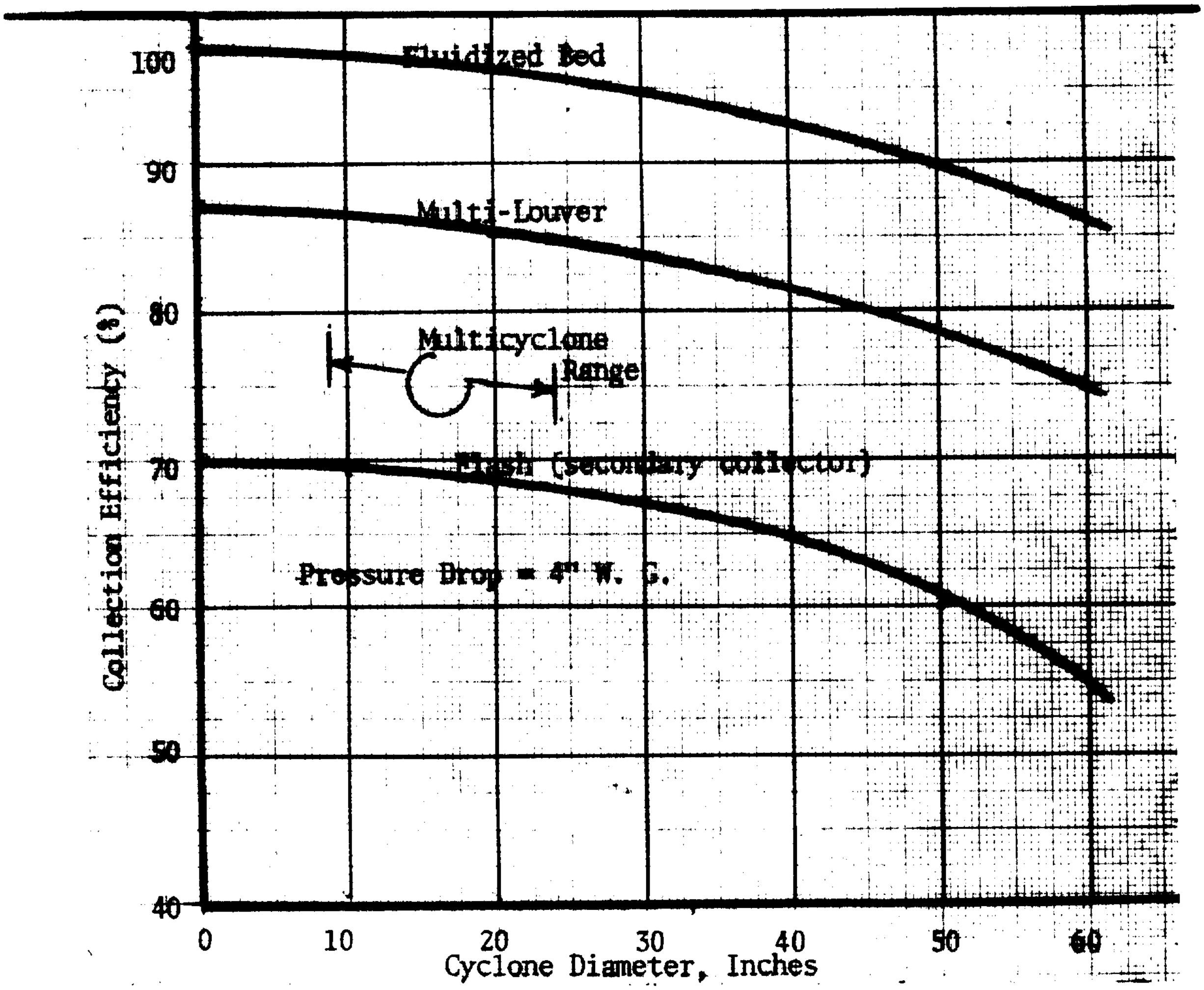


Figure 6. Relation between Cyclone Diameter and Collection Efficiency

APPENDIX
THERMAL COAL DRYERS

Type of Thermal Dryer	Emission Factor* lbs of particulate/ ton of coal dried	Reference Number
Fluidized Bed	5	4
	4	4
	10	5
Flash	4.5-8	4
	3.8	5
	4.7	5
Multilouvered	6.5	6
	8.5	6

*Particulate Emission Factor is the particulate from cyclone collector.

Reliability of Emission Factors

Table IIIa lists rankings of emission factors of Table II on a scale of reliability based on a maximum point value of 40.

Table IIIa. Ranking of Emission Factors

	Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total 0-40
Fluidized Bed	12	8	5	25
Flash Dryer	15	8	5	28
Multilouvered Dryer	12	8	5	25

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EXPLOSIVES MANUFACTURING

BACKGROUND

An explosive is a material which, under the influence of thermal or mechanical shock, decomposes rapidly and spontaneously with the evolution of large amounts of heat and gas.[7] Currently, over 1 million tons of explosives are used in the United States each year for industrial purposes.[8] Military explosives consumption rates are classified; currently, they exceed industrial usage by a considerable factor.

Chemical explosives are generally classified into two major groups; high explosives and low explosives. High or detonating explosives are further divided into either primary or secondary types. Primary high explosives, such as lead azide, mercury fulminate and nitromannite, are initiating or detonating types which can be made to explode by the application of fire or by means of a sharp blow. Secondary high explosives, which are insensitive to both mechanical shock and flame but explode when set off by detonation of a primary high explosive, include trinitrotoluene (TNT), ammonium picrate, and picric acid. Low or deflagrating explosives do not explode but burn; examples are black powder and nitro-cotton.[7] Table IV lists the common explosives and ingredients used in United States explosives industry.[10]

PROCESS DESCRIPTION

Although many different types of explosives are manufactured in the United States for both military and industrial consumption, three major types account for nearly all of the annual production. These are: (1) ammonium nitrate blasting agents, (2) nitroglycerin and dynamites, and (3) TNT. Table V lists ingredients and their quantities in United States Industrial Explosives for 1967.[12]

Ammonium Nitrate Blasting Agents

There are two major classifications of ammonium nitrate blasting agents: ammonium nitrate - fuel oil blasting compounds, and water slurry - ammonium nitrate blasting agents. Ammonium nitrate is simply made by neutralizing nitric acid with ammonia:[8]

TABLE IV. COMMON EXPLOSIVES AND INGREDIENTS USED IN U. S. EXPLOSIVES INDUSTRY[10].

MATERIAL	APPLICATION	
	Military	Industrial
Primary High Explosives		
Mercury fulminate	x	x
Lead azide	x	x
Diazodinitrophenol	x	x
Nitromannite	x	x
Secondary High Explosives		
TNT (Trinitrotoluene)	x	x
Tetryl (trinitrophynyl-methylnitramine)	x	x
RDX (cyclotrimethylene-trinitramine)	x	
PETN (pentaerythritol tetranitrate)	x	x
Ammonium picrate	x	
AN (Ammonium nitrate)	x	x
Picric acid	x	
DNT (dinitrotoluene)	x	x
EDNA (ethylene diamine dinitrate)	x	
NG (nitroglycerine)		x
Nitrostarch		x
Low Explosives		
Smokeless powder	x	x
Nitrocotton	x	x
NG (nitroglycerine, inerted)	x	x
DNT (dinitrotoluene ingredient)	x	x
Black powder (sulfur, charcoal, and sodium or potassium nitrate)	x	x
Non-Explosive Ingredients		
Aluminum	x	x
Other metals (ferrosilicon, etc.)		x
Metal nitrates	x	x
Waxes and paraffins	x	x
Mononitrotoluene	x	
Other combustibles		x
Diphenylamines, other hydrocarbons		x
Wood pulps, meals		x
Chalk, sulfur, carbon		x

Table V. Ingredients in U.S. Industrial Explosives, 1967[12]

Ingredient	Quantity, tons
Ammonium Nitrate	
Processed and unprocessed	643,000
In permissibles [a]	23,000
In other high-explosives[a]	53,000
In other blasting agents[a]	76,000
Total Ammonium Nitrate	795,000
Fuel Oil, Carbonaceous Material and Other Non-Explosive Ingredients	120,000[b]
Nitroglycerine	28,000[b]
TNT	10,000[b]
Total	953,000

[a] Ammonium nitrate estimated at 65 percent of permissible, 35 percent of other high explosives and 60 percent of water-gels and slurries and rigidly cartridged blasting agents.[10,14]

[b] Estimates provided by Du Pont.

$NH_3 + HNO_3 \rightarrow NH_4\ NO_3$

Ammonium nitrate explosives manufacture consists of blending the ammonium nitrate with vehicles, fuel oil, or water, and other minor constituents such as powdered aluminum, gels, and various organic materials. Most of these materials tend to desensitize the ammonium nitrate.

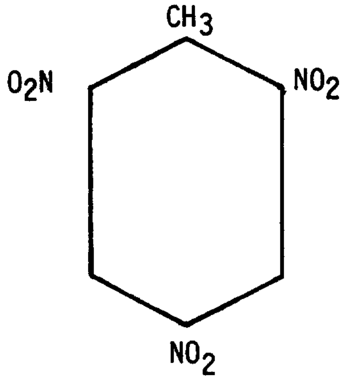
Emissions resulting from the manufacture of ammonium nitrate are discussed in greater detail in the section on nitrate fertilizers.

Nitroglycerin and Dynamite

Nitroglycerin was the first high explosive to be employed on a large scale. It is made by the nitration of glycerin, in which glycerin of high purity (+99.9%) is slowly added to mixed acid having the approximate composition 59.% H_2SO_4, 40% HNO_3, and 0.5% H_2 . For easier and safer handling, nitroglycerin is usually manufactured into dynamite. Modern dynamite generally uses wood flour, ammonium nitrate, or sodium nitrate to absorb the nitroglycerin, to which an oxidizer is added.[7] Figure 7 outlines the manufacture of nitroglycerin and dynamite.

TNT

Although many new explosives have been developed since the start of World War II, symmetrical trinitrotoluene (TNT)



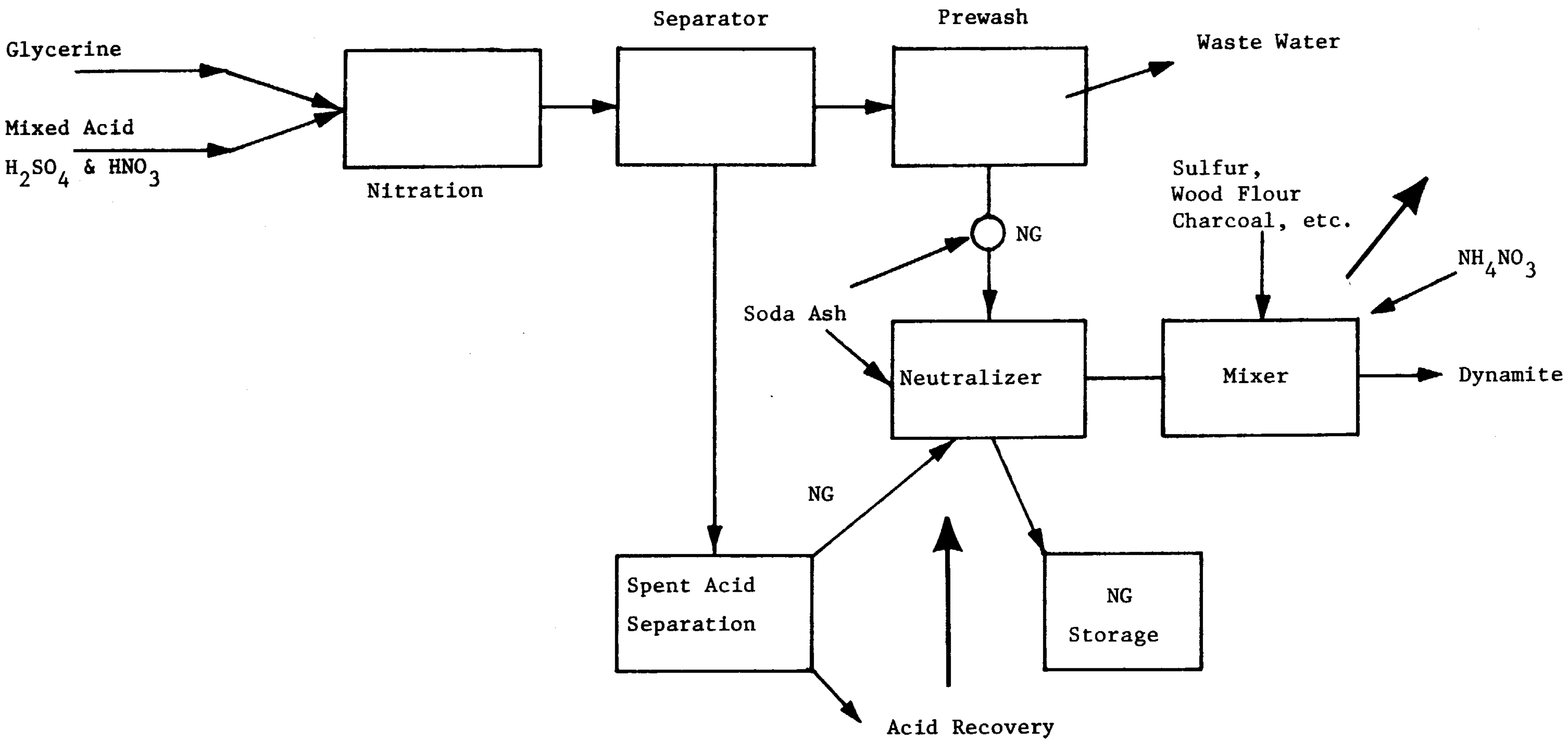


Figure 7. Simplified Flow Diagram for Nitroglycerine and Dynamite Manufacturing Process[12]
Major Emission Points Are Marked by Heavy Arrows

is still the most important military high explosive used in the United States. TNT is made by three-stage nitration of toluene with mixed acids (commonly 82.7% total sulfuric acid and 23.3% nitric acid). The crude TNT, or "tri-oil", is purified for military use by a water and soda ash wash, followed by a sellite (acidulated 16% Na_2SO_3) or oleum ($H_2SO_4 \cdot SO_3$) sellite wash. Water and soda ash neutralize the excess acid, while the sellite reacts preferentially with the unsymmetrical TNT to produce water-soluble dinitro sulfonales.[7] The wash waste (commonly called red water) from this purification process is either discharged directly into a stream or sewerage system or is concentrated to a slurry and incinerated. Production of TNT for industrial use does not require the final purification wash, so no red water is discharged. Figure 8 illustrates the multistage operation of the TNT manufacturing process.

FACTORS AFFECTING EMISSIONS

The most important factor affecting emissions from the manufacture of explosives is the efficiency of the manufacturing process, which is generally related to the sensitivity of the explosive being made. In addition, the degree to which the acids (nitric and sulfuric) are exposed to the atmosphere during the manufacturing process determines emissions of NO_x and SO_x. The type and efficiency of control devices in use, if any, also affect emissions.

EMISSIONS

Although very little information exists on atmospheric emissions from explosives manufacturing plants, the quantities of pollutant emissions from the actual explosives processes are believed to be quite small. Some emissions originate during the preparation of materials such as oleum-sellite that is usually done at the TNT plant. Nitric and sulfuric acid, for which emission factors are given in previous sections of the report. Red water from the manufacture of TNT is usually a water pollution problem, but when it is concentrated and incinerated some pollutants are emitted. Table VI presents the emissions from the various processes involved in making TNT and nitrocellulose. More detailed emission data are developed in the Appendix.

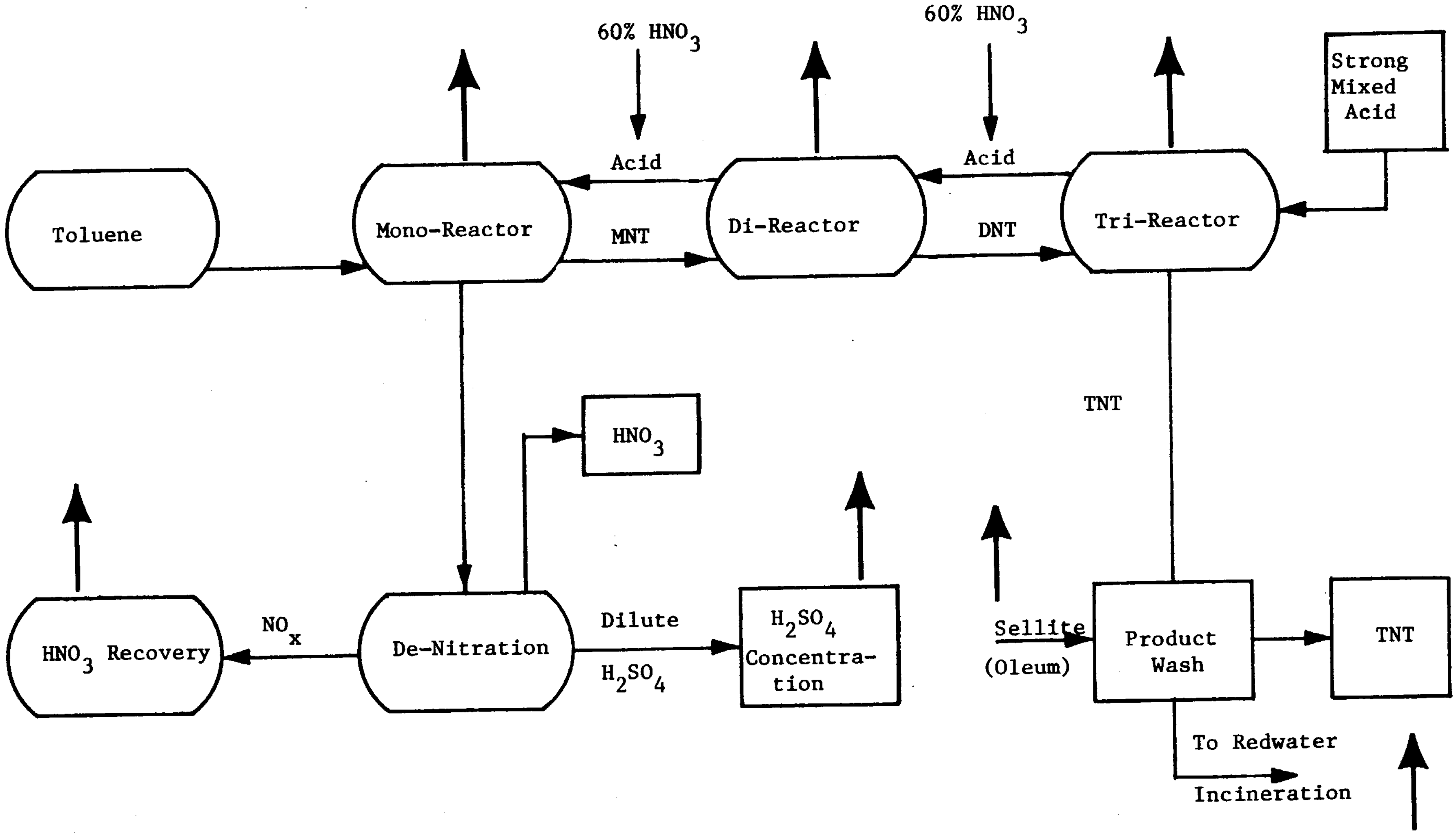


Figure 8. Trinitrotoluene (TNT) Manufacturing Diagram
(Major emission points are marked in heavy arrows.)

Table VI. Emission Factors for Manufacture of Explosives

Product and Process	Emission: lbs/ton of Product (uncontrolled, except as noted)		
	NO_x[a]	SO_x[b]	Particulates
High Explosives			
Nitroglycerine			
Acid Recovery	X	X	-
Dynamite Preparation	X	-	-
TNT (see Appendix)			
Nitration Reactor Line	160[c,d]	-	-
Nitric Acid Concentrator	1	-	-
Sulfuric Acid Concentrator	2[e]	18[c,e]	0.4[c]
Red Water Incinerator[f]	6[g,h]	13[h]	50[c,h]
Low Explosives			
Nitrocellulose (see Appendix)			
Reactor Pots	12.5	-	-
Sulfuric Acid Concentrator	29[i]	65[j]	-

[a] Expressed as NO_2

[b] Expressed as SO_2

[c] Based on unpublished stack test data, NAPCA Office of Criteria and Standards

[d] With 90% to 95% efficient bubble cap absorption system, one plant reported 2.5 lb/ton. Recommended emission factor for average control systems is 10 lb/ton. Uncontrolled factors up to 213 lb/ton have been reported.

[e] After precipitator and spray chamber 2 lb. NO_2/ton and 4.2 lb. SO_x/ton reported. Approximately 50% of SO_x is emitted as SO_2.

[f] Not used for making industrial TNT

[g] Unpublished stack test data (Note c) show NO_x emission density of 1360 ppm, from flow of 4500 scfm.

[h] From plant producing 400 tons TNT/day. Particulate emission factor for this plant is 70 lb/ton

[i] Reported range, 17 to 40 lb/ton

[j] Reported range, 49 to 81 lb/ton

[x] Emissions noted, but no estimates available

APPENDIX

NITROCELLULOSE

Sulfuric acid Concentrator - Uncontrolled Emissions

Report emissions[15] - Volume 17,800 scfm

SO_2 270 ppm ± 25%

NO_x 170 ppm ± 40%

Plant capacity = 18 tons/day of nitrocellulose

SO_2:

$$17{,}800 \frac{ft^3}{min} \times 270 \times 10^{-6} \times \frac{64 \text{ lbs/lb-mol}}{380 \text{ ft}^3\text{/lb-mol}} \times 1440 \frac{min}{day} = 1170 \frac{\text{lbs } SO_2}{day}$$

1170 ÷ 18 tons product/day = 65 lbs/ton ± 25%

NO_x:

$$17{,}800 \frac{ft^3}{min} \times 170 \times 10^{-6} \times \frac{46}{380} \times 1440 = 530 \text{ lbs } \frac{NO_2}{day}$$

530 ÷ 18 tons product/day = 29 lbs/ton ± 40%

Acid mist not reported, but an electrostatic precipitator was used at this plant.

Reactor - 3800 scfm, 340 ppm, emission - 225 lb/day or 12.5 lb/ton of product

TNT MANUFACTURE

Emission data reported from plant with 400 ton/day production rate, ± 25%.[16]

Nitration Line

85,513 lbs NO_2/day after scrubbers or 213 lbs/ton of TNT. A modern plant emitted only 2.5 lbs/ton[12]. Use 10 as an average factor.

Red Water Incinerator

NO_x - 2508 lbs/day or 6.1 lbs/ton of TNT

SO_x - 5223 lbs/day or 13 lbs/ton of TNT

1% of SO_x is SO_3

Particulate

28,300 lbs/day or 71 lbs/ton of TNT

Sulfuric Acid Concentrator

NO_x - 950 lbs/day or 2.4 lbs/ton of TNT

SO_2 - 944 lbs/day or 2.4 lbs/ton of TNT

SO_3 -1070 lbs/day or 2.7 lbs/ton of TNT (equivalent to 1.8 lbs as SO_2)

Oleum - Sellite

1263 lbs SO_2 or 3.16 lbs/ton of TNT

383 lbs H_2SO_4 or 0.9 lbs/ton of TNT

Nitric Acid Concentrator

NO_x - 434 lbs/day or 1.1 lbs/ton of TNT

Reliability of Emission Factors

Table VIa lists rankings of emission factors of Table II on a scale of reliability based on a maximum point value of 40.

Table VIa. Ranking of Emission Factors

	Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total 0-40
TNT				
Nitration Reactor Line	12	3	2	17
Nitric Acid Concentrator	10	3	2	15
Sulfuric Acid Concentrator	10	3	2	15
Red Water Incinerator	10	3	2	15
Nitrocellulose				
Reactor Pots	15	5	8	28
Sulfuric Acid Concentrator	15	5	8	28

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12. "Control Techniques for Nitrogen Oxide Emissions from Stationary Sources." National Air Pollution Control Administration Publication No. AP-67, March, 1970. p. 7-21 to 7-24.

13. Ibid., p. 7-41.

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FERROALLOY PRODUCTION

Ferroalloys is the generic term for alloys consisting of iron and one or more other metals. Ferroalloys are used in steel production as alloying elements and deoxidants. Table VII lists the more commonly used ferroalloys and the amounts produced annually in the United States. Production figures for alloys containing aluminum and calcium are included under "All others".

Table VII. Electric Furnace Production of Ferroalloys in the United States 17, 1967 (tons/year)

Ferroalloy	Production
Ferromanganese	280,000
Ferrosilicon	528,000
Ferrochromium	263,000
Ferrochromsilicon	154,000
Ferrophosphorus	111,000
Silicomanganese	230,000
All Others	259,000
TOTAL	1,825,000

Ferroalloys are made by reduction of suitable oxides in an electric arc furnace. For ferrosilicon the charge consists of iron scrap, silica, and coke; and the chemical reaction is as follows:

$$Fe_x + SiO_2 + 2C \rightarrow Fe_xSi + 2CO$$

Figure 9 shows a diagram of an electric furnace used in this process. Between 150 and 200 electric furnaces for making ferroalloys are in operation at about 50 plant locations through the United States. In this country, 75 percent of the ferroalloys are produced in open furnaces and 25 percent in semi-covered furnaces. Completely sealed furnaces are in use in other countries. A very small amount is made in blast furnaces, but this method is not suitable for general use because of the difficulty in reaching high temperatures necessary to smelt most alloying materials. Figure 10 shows a typical semi-covered furnace.

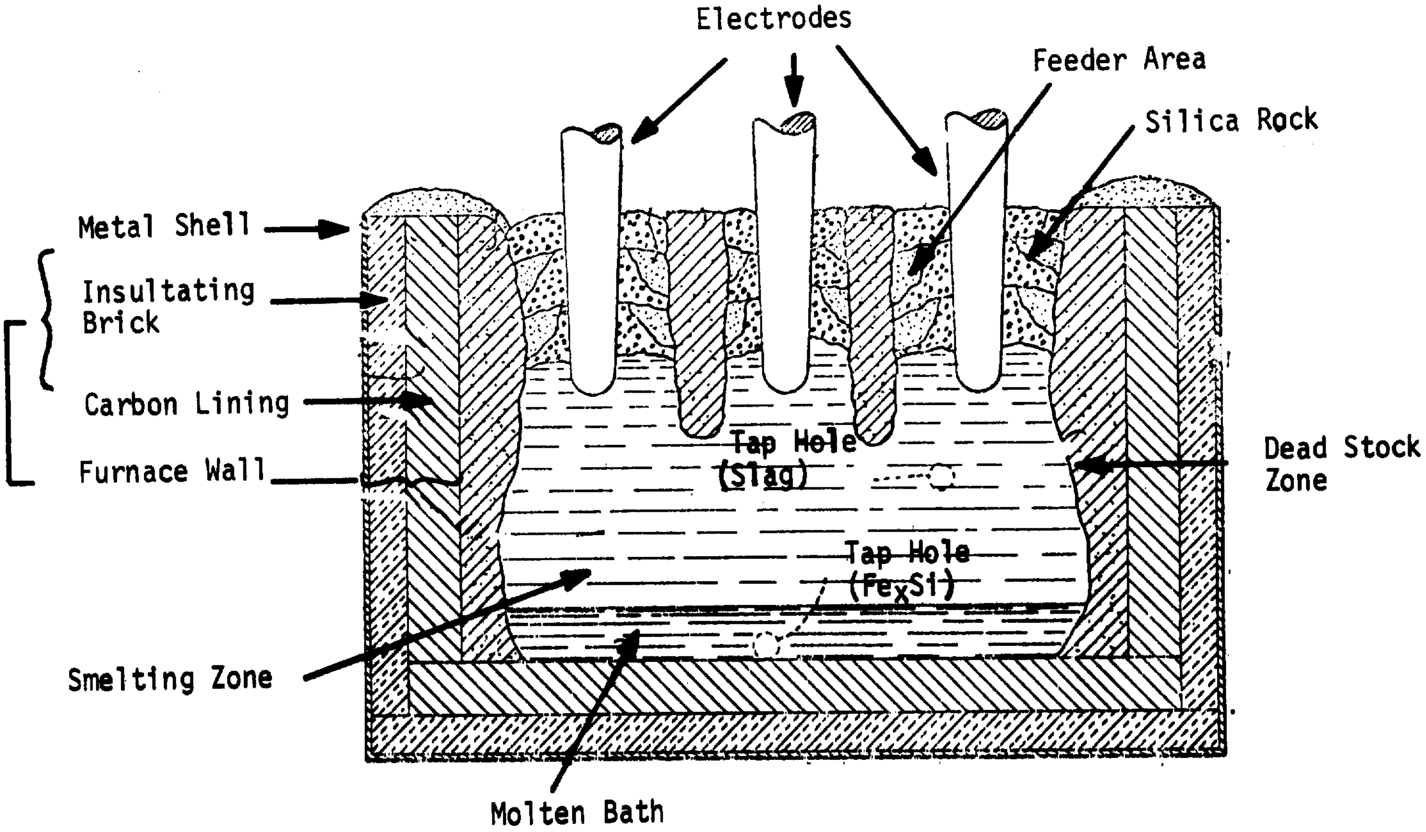

Figure 9.[17] Vertical Section of a Ferrosilicon Producing Electric Furnace

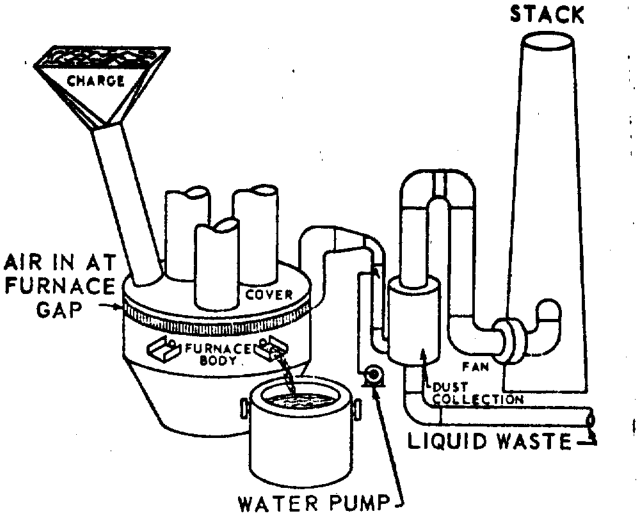

Figure 10. Electric Furnace for Ferroalloys Industry

EMISSION SOURCES

The major source of emissions (about 95% of the total) is above the furnace itself. Small amounts are emitted during tapping and related operations and during sizing and crushing of the product.

The smelting mechanism leads to the evaporation of high vapor pressure metals and metal oxides at temperatures from 2000-2500°C. Iron, manganese, silicon and silicon dioxide evaporate in the region of the electrodes. There are many small electric arcs between the electrodes and the charge. Smelting proceeds rapidly at high temperatures in the small area surrounding the lower end of the electrodes.

The open type of electric furnace is the oldest, simplest, and most widely used. The three primary ferroalloys, silicon based, manganese based and chromium based are produced in open furnaces. All except silicon metal are also produced in semi-closed furnaces. Calcium carbide which is not a ferroalloy is an important by-product of associated ferroalloy operations. Table VIII shows a breakdown of production percentages for the three major ferroalloys and calcium carbide.

Table VIII. Percentage of Production for Primary Ferroalloys

Type	Percent of Total Production
Silicon Based Alloys	
90% FeSi	40%
75% FeSi	
65% FeSi	
50% FeSi	
25% FeSi	
CaSi	
Manganese Based Alloys	
FeMn	25%
SiMn	
Medium carbon FeMn	
Low carbon FeMn	
Chromium Based Alloys	
FeCrSi	25%
High carbon FeCr	
Low carbon FeCr	
Calcium Carbide	10%

Most furnaces are of the submerged-arc type in which the electrodes are directly in the metal, as shown in Figure 9. The open-arc type in which the electrodes are just above the surface is used only in refining and is not considered here.

A modern, open furnace is usually equipped with a hood to collect the gases. Temperature of the escaping CO may exceed 750°F, and some of the gas burns when it mixes with entrained air. Adequate ventilation is necessary in the furnace areas to hold CO levels within safe limits. CO monitors are employed to warn of buildup of hazardous concentrations. Escaping gas which includes particulates and unburned CO is vented from the hood through a particulate control device and up the stack. The CO pollution problem is usually handled by flaring; but the particulates, which are essentially submicron in size, are difficult to control. Reportedly, ferromanganese gases are much easier to clean than the gases from ferrosilicon furnaces. The silicomanganese fume, which has lower electrical resistivity and higher specific gravity than does the ferrosilicon fume, is also easier to collect.

The chemical equation shows that for each mol of ferroalloy, which varies in weight from 84g to 111 g depending upon its composition, 56g of carbon monoxide occupying a volume of 44.8 liter N.T.P. is produced. This is the equivalent of 12,950 cf of CO per ton of ferromanganese and 17,100 cf of CO per ton of ferrosilicon. This gas escapes through the pores and channels in the charge. Large quantities of particulates and dilution air are entrained in the escaping gas. The total flow of escaping gases may range from 400,000 acfm to 700,000 acfm depending on the quantity of infiltrating air. Closed or semi-closed furnaces emit smaller quantities of gases. However, enclosing an open furnace to reduce the secondary air results in damages from high gas temperatures and leads to difficulties such as restricted operator access. Experiments indicate that problems with fully closed furnaces will not soon be resolved.

FACTORS AFFECTING EMISSIONS

The particle size of the charge material has a vast effect upon the formation of the metallurgical fume. A dense charge with many fines will cause gases to be emitted from few channels near the electrodes. This channeling will produce an increase in temperature and velocity and cause eruptions. Vaporization and entrainment of fines will be increased. A porous charge will give good gas distribution. Use of good quality scrap will reduce emissions.

Dust content in the fume depends on the type of production and raw materials used. Even in the same product, content varies considerably according to the condition of the furnaces.[19]

FERROSILICON

Ferrosilicon is an alloy of iron and silicon. The alloy composition is indicated by the percentage of silicon. Raw materials for the production of ferrosilicon are quartz (SiO_2), iron (usually iron ore or scap), and coke, charcoal or coal. Electric furnaces for the production of ferrosilicon range in size from 5,000 KW to 40,000 KW.

Silicon metal, containing approximately 99 percent silicon, is manufactured in the same manner as the other ferrosilicon alloys. Silicon metal contains 0.2 - 1.0 percent iron and minor percentages of other metals. Raw materials for silicon production are quartz rock (SiO_2), wood chips, and coal.

As the silicon content of the alloy increases, the frequency of eruptions within the furnace increases. Eruptions increase the emissions from the furnace. Satisfactory operation of ferrosilicon furnaces demands that eruptions be efficiently counteracted. Careful operation and attention are extremely important.

The fine fume that is emitted consists mainly of amorphous silicon dioxide (SiO_2). Particle size distribution is approximately:

20 percent greater than one micron
30 percent 0.1 to 1.0 microns
50 percent less than 0.1 micron

Approximately 10-20 percent of the particulate emission is a coarse fraction consisting of materials from the charge.

The plume from the process is very conspicuous. Complete elimination of the plume requires collection equipment of efficiency in excess of 95 percent. This corresponds to an outlet grain loading of 0.02 grains per standard cubic foot.[19] Inlet grain loadings may be 0.35 to 2.1 grains per standard cubic foot.

FERROMANGANESE

Ferromanganese alloyws contains manganese, riron, and small amounts of carbon and silicon. The following alloys are produced in ordinary blast furnaces:

- Alloys with a low manganese content

  5 - 20 percent manganese
  3 1/2 - 5 percent carbon
  15 - 20 percent manganese
  10 percent silicon
  5 percent carbon

- Alloys with a high carbon content

  78 percent manganese
  7 percent carbon
  2 percent silicon
  13 percent iron

Ferromanganese alloys of high (>1.5 percent), medium (1.0 - 1.5 percent), and low (0.1 - 0.3 percent) carbon contents are produced in electric furnaces.

Manganese tends to evaporate due to its low vapor point. Hence, process emissions will contain evaporated manganese (approximately 5 - 10 percent of the Mn charged) and a coarse fraction (about 20 percent of the particulate emission) of coke breeze and manganese ore from the charge. The fine fraction of the particulate emission is fume with a particle size of 0.1 - 1.0 microns. Average particulate concentration in the emitted gases is 7 - 17 grains per standard cubic foot.

FERROCHROMIUM, SILICOMANGANESE, FERROSILICOCHROME

The air pollution problems associated with the production of ferrochrome, silicomanganese, and ferrosilicochrome are essentially the same as the problems associated with the production of ferrosilicon. These alloys are produced mainly in open electric furnaces. A minor amount of silicomanganese is produced in closed furnaces.

The commonly produced ferrochromium alloys contain 60 - 70 percent chromium, 4 - 6 percent carbon, and less than 2 percent silicon. Other alloy compositions are produced as ordered.

Silicomanganese is used mainly as a deoxidant in the production of steel. It is also used as a reducing material in the production of ferromanganese, which has a low carbon content. Silicomanganese which contains 15 - 25 percent Si is produced from manganese slag or low-grade manganese ore, quartz, and coke breeze. The fume from this operation has a pronounced reddish brown color. Since manganese compounds are poisonous, process emissions present a health hazard. To eliminate the visible plume, very high collection efficiency equipment is required.

Chromium in ferroalloy production behaves similarly to manganese. Since chromium has a low vapor pressure, there is very little loss of material due to vaporization. Chromium will be emitted from the process as larger particles of raw materials which are entrained in the gas stream.

EMISSION FACTORS

Very little information on ferroalloy production has been found in the open literature; published data on emissions from open and closed (or semi-closed) furnaces are, therefore, sparse. A compilation of emission factors that appear in available references, including company proprietary stack test reports, appears in the Appendix. From this list, Table IX was developed. Emissions factors in this table are recommended as representative of the best available engineering judgment at this time.

No emission factor for carbon monoxide appears in the references. Emissions are known to vary considerably from plant to plant depending upon the ferroalloy being produced, the type and capacity of furnace, provisions for containment of waste gases, and the efficiency of the carbon monoxide combustion process, whether flared or recycled for use as fuel. Emission factors that appear in Table IX are estimates based upon the assumption that 10 percent of the carbon monoxide produced by open furnaces escapes into the atmosphere. Half of this percentage is assumed to be residual from all the combustion processes to which the gases are subjected. The other half is assumed to escape into the shed which houses the furnace, and is exhausted through the ventilation system. For closed furnaces, the emission is assumed to be 3 percent, all residual, the amount escaping into the shed assumed to be negligible. Computations which provide the basis for the estimates are shown in the Appendix.

Table IX. Emission Factors for Ferroalloy Production (pounds/ton of product)

Product	Emission Factor (pounds/ton of product)	
	Particulates (before control)	Carbon Monoxide (residual & escaping)
Open Furnaces		
50% FeSi	200	133
75% FeSi	315	160
90% FeSi	565	182
Silicon metal	625	---
Silicon manganese	195	---
FeMn	---	101
FeCr	---	104
Closed Furnaces		
50% FeSi	---	40
75% FeSi	---	48
90% FeSi	---	54
FeMn	45	30
FeCr	---	31

The key subsystem of this process is the electron beam accelerator. Control of this unit's power supply is based upon inlet composition, flow rate, and temperature of the flue gas. (The penetration of the gas stream by the beam requires a unique discharge pattern and other special design considerations.) A powder containing both ammonium nitrate and sulfate is generated by an unknown reaction mechanism. The gas is then passed through a second ESP to remove the solid by-product. The by- product treatment system is still being developed. Various methods being investigated include thermal decomposition in the presence of an inert gas, steam roasting with CaO, or steam roasting with H_2O. The byproduct may eventually be useful as a fertilizer.[150]

The Ebara Manufacturing Company in conjunction with Japan Atomic Energy Research Institute (JAERI) has operated a 1000 Nm^3/hr pilot plant treating flue gas from an oil-fired boiler. In 1976, Ebara began operating a 3000 Nm^3/hr pilot plant on the off-gas from an iron ore sintering furnace at Nippon Steel. This process is licensed in the U.S. by Avco- Everett Research Laboratory. The U.S. Department of Energy (DOE) is funding development of an electron beam process offered by Research- Cottrell. Pilot unit tests with flue gas are scheduled, however, the details of the program are not yet available.

4.5 PRE-COMBUSTION TECHNIQUES FOR PM, NO_x, AND SO_2 CONTROL

Pre-combustion techniques considered for reducing PM, NO_x, and SO_2 emissions from industrial boilers include the use of naturally occurring clean fuels, physically or chemically-cleaned fuels, and synthetic (coal-derived liquid or gaseous) fuels. A technique for reducing particulate emissions from oil-fired industrial boilers, involving use of an oil/water emulsion, is also considered as a pre-combustion emission control technique.

Naturally-occurring clean fuels discussed in this section are raw low sulfur coal and raw low sulfur oil which are low enough in sulfur content to meet SO_2 emission limits with no additional controls. The fuel cleaning processes discussed in this section are physical coal cleaning (PCC) and hydrodesulfurization (HDS) of oil. These processes are primarily designed

$$\text{Emission} = 10\% \text{ of ratio } \frac{56}{\text{unit weight of ferroalloy}}$$

$$\text{For: } 50\% \text{ FeSi} = \frac{5.6}{84} = 6.67\% = 133 \text{ pound/ton}$$

$$75\% \text{ FeSi} = \frac{5.6}{70} = 8.00\% = 160 \text{ pound/ton}$$

$$90\% \text{ FeSi} = \frac{5.6}{61.6} = 9.09\% = 182 \text{ pound/ton}$$

$$\text{FeMn} = \frac{5.6}{111} = 5.05\% = 101 \text{ pound/ton}$$

$$\text{FeCr} = \frac{5.6}{108} = 5.18\% = 104 \text{ pound/ton}$$

Reliability of Emission Factors

Table IXa lists rankings of emission factors of Table II on a scale of reliability based on a maximum point value of 40.

Table IXa. Ranking of Emission Factors

	Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total 0-40
Open Furnaces				
Particulates	15	8	7	30
CO	15	8	7	30
Closed Furnaces				
Particulate	8	4	3	15
CO	15	8	7	30

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NITRATE FERTILIZERS

Nitrate fertilizers are here defined as manufactured salts of nitric acid with a strong base, for use as agricultural fertilizers in pure form, in mixtures, or in derivative compounds such as nitrophosphates. The most important product in this category is ammonium nitrate. Nitrates of potassium and calcium are also manufactured, but on a much smaller scale. Data on emissions from nitrates other than ammonium nitrate are not available, although emissions of nitrosyl gases, nitrogen oxide, and volatile intermediate products are known to occur. Details on the ammonium nitrate process that are here described may therefore be considered as representative for the other nitrate ferilizers as well.

PROCESS DESCRIPTION

Ammonium nitrate is produced by the reaction of anhydrous ammonia, NH_3, with nitric acid, HNO_3, in concentrations of 57%-65%(21,35). The reactants are brought together in a neutralizer that may be at atmospheric pressure or up to 50 to 60 psi. At least one unit [35] is operated under vacuum in an attempt to obtain the best balance between operation, corrosion and use of the available heat of formation to concentrate the product solutions. The basic reaction is:

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3 + \text{heat}$$

A slight excess of ammonia is employed in the neutralizer but the vapors are scrubbed by a recirculating stream of ammonium nitrate solution. Nitric acid may be sprayed into the vapors at the inlet to the scrubber in order to neutralize any free ammonia. Typical concentrations of 80%-85% are produced at this stage. The ammonium nitrate solution may be transferred to storage from any suitable point in the process for subsequent sale as is or in combination with other liquid fertilizer materials.

Two basic processes are used to form ammonium nitrate pellets ("prills") or granules for marketing. Simplified flow diagrams for the two processes are shown in Figures 11 and 12(28,29,38).

Figure 11 shows the process utilizing a prilling tower for pelletizing ammonium nitrate. The product passes from the reactor to an evaporator or concentrator, where through the action of a falling film and/or a vacuum it is concentrated to 95% or more. The design height of the prilling towers is an inverse function of the percentage concentration.[37]

In the prilling tower, concentrate is sprayed in near the top, and in falling comes in contact with a rising jet of cool air. Ammonium nitrate slurry droplets solidify into spherical pellets as they fall. Limestone may be added to the ammonium nitrate solution before prilling to produce calcium ammonium nitrate(25,28,29).

Figure 12 shows the alternate procedure, which uses ordinary rotating pan and drum granulators. In this process, "fillers" and normal or triple superphosphate are added to aid in the granulation process and increase the plant food value of the product.

The products of both processes are usually dried and cooled, then sized by screening. Over- and undersized material is recycled to appropriate points in the process. Specification grade pellets are coated with clay or diatomaceous earth to prevent sticking.

The major points of emissions in both processes are in the drying and cooling operations. Lesser amounts may be emitted from the reactor and concentrator, and from the prilling tower or granulator. Most emissions are particulates, but ammonia gas may escape anywhere along the process and volatile nitrosyl gases[22] may be emitted from areas where ammonium nitrate is stored. Since nitrosyl presents an extreme hazard, operators generally try to minimize formation and escape of these gases by tight control over the manufacturing process.

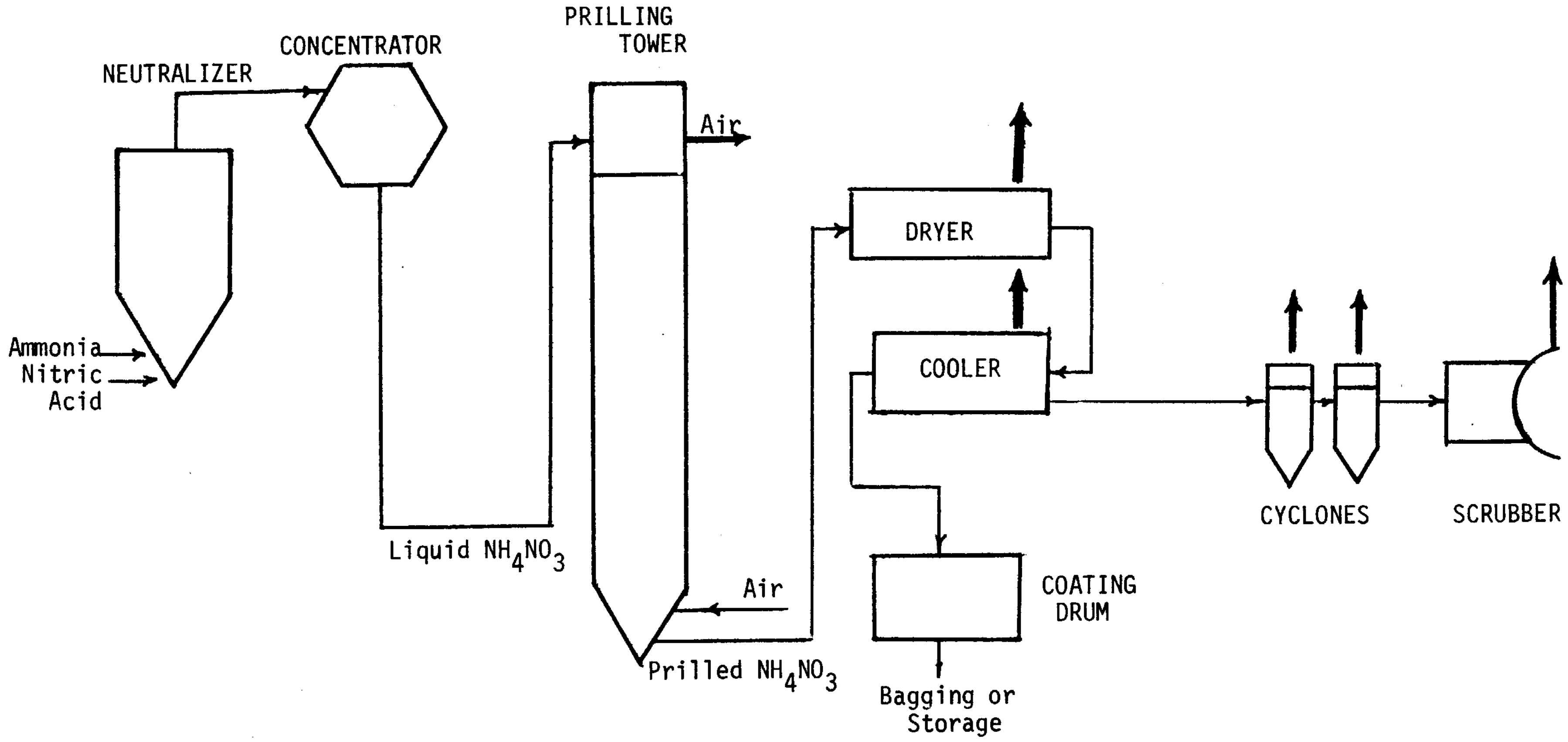

FIGURE 11. Simplified Flow Chart of Prilled Ammonium Nitrate (Emission Points shown by Heavy Arrows)

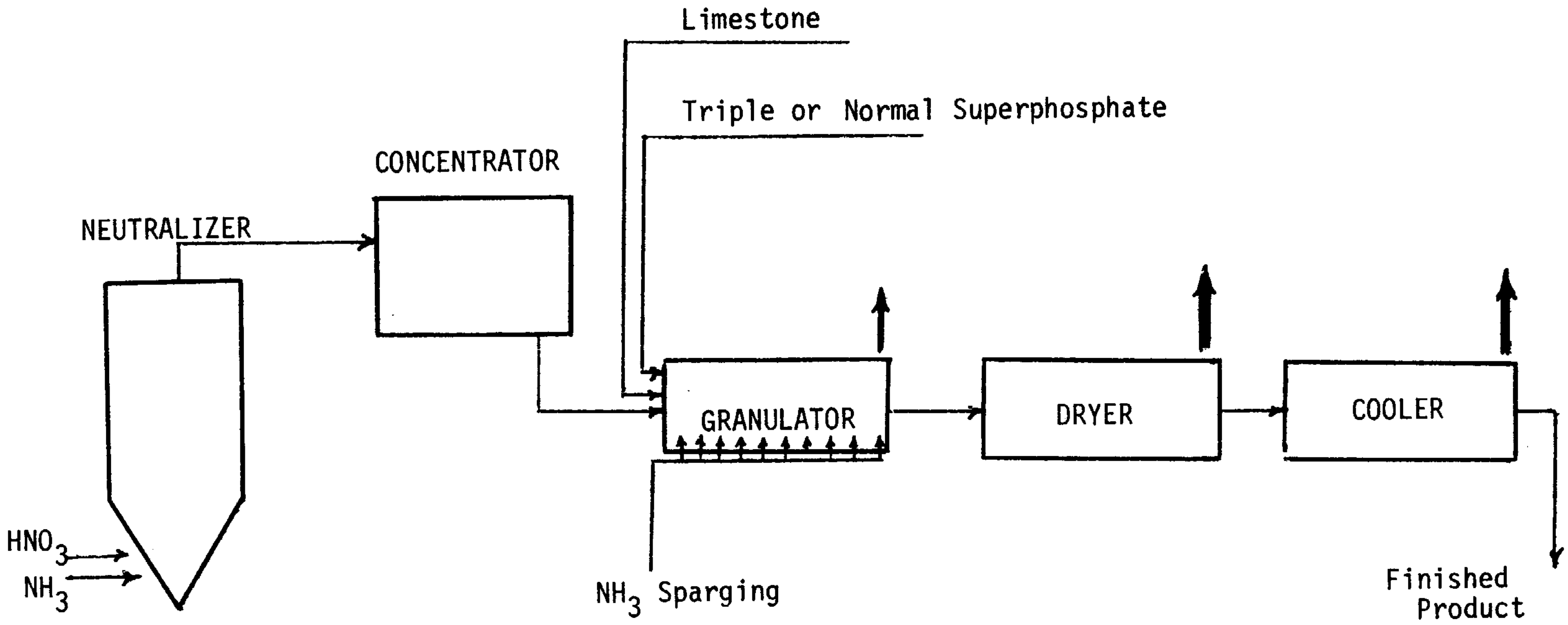

FIGURE 12. Simplified Flow Chart of Granulated Ammonium Nitrate (Emission Points shown by Heavy Arrows)

FACTORS AFFECTING EMISSIONS

Differences in the processes and/or equipment for producing nitrate fertilizers may affect the type and amount of emissions. One factor is good housekeeping throughout the process, thus to minimize escapage and to operate more economically. As an example, sealing a pressurized neutralization reactor allows escaping gases to be carefully controlled by a recycle scrubbing device. Leaks are usually visible. Even in the unpressurized reaction vessel, where small leaks might go unnoticed, scrubbing and collection of escaping gases is economically advantageous. An estimated 1 to 3 percent of the ammonia [30] might escape the neutralizer but most of this can be recovered in the recycle scrubber. No nitrogen oxides appear to be lost from the process.

A second factor is the use of a vacuum for the neutralizer. In the vacuum process ammonia and entrained ammonium nitrate that escape through the heat exchangers, recycle coolers, etc., are absorbed by the condensing water in the barometric condensers and thus not released to the atmosphere.

A third factor is the use of collectors. Nitrate dust or particulate matter are produced in the granulation and prilling operations. Particulate matter is also produced in the drying, cooling, coating and material handling operations. The coating materials, such as clay or diatomaceous earth, are emitted as particulate material because of normal handling problems coupled with their very small particle size. Additional dust may escape from the bagging and shipping facilities.

Typical operations do not use collection devices on the prilling tower. Wet or dry cyclones are employed for various granulating, drying or cooling operations in order to recover valuable product. Wet scrubbing sometimes follows the cyclones. At least one manufacturer is planning to install a collection device on the product handling system.

EMISSIONS

Table X lists the emission factors for the various steps in nitrate fertilizer processes. All data are derived from unpublished source tests [34] shown in the Appendix. No results of source testing from ammonium nitrate production facilities have been reported in the literature. TVA is currently conducting a survey on nitrophosphate emissions but results are not yet available [39].

A check on these factors was made through a material balance calculation. Two independent sources(32, 33) concur in regard to an overall plant operating yield. There is very little difference in the yields between various processes. Ordinary ammonium nitrate processing results in a yield of approximately 97 percent, calcium ammonium nitrate a yield of 97-97.5 percent, and granulated 8-16-0 nitrate fertilizer a yield of 96.5-97 percent. Based on these yields, it is evident that most of the losses are into waste water and only a small part is emitted into the atmosphere.

TABLE X EMISSION FACTORS FOR NITRATE FERTILIZER MANUFACTURING

Particulate Emission

Type Operation	Total	(lbs./ton product - uncontrolled) NO_3	NH_3	P_2O_5	F^-
1. Prilling[b,d]					
Prilling Tower	0.86	0.86	neg.	--	--
Pre Dryer	1.7	1.7	neg.	--	--
Secondary Dryer	0.017	0.017	neg.	--	--
Cooler	10.2	10.2	neg.	--	--
2. Granulation [c,d,f]					
Granulator	0.43	0.08	0.44	0.002	0.001
Dryer	3.89	1.49	0.14	0.030	0.033
Cooler	3.33	1.27	0.13	0.047	0.044

(a) Emissions negligible from the neutralizing and concentrating steps of process.

(b) General practice of industry.

(c) At least one manufacturer uses granulation instead of prilling.

(d) Without limestone addition.

(e) Cyclones or dryers and coolers will reduce factor an estimated 70%. Actual emission data on cyclones followed by a wet screen scrubber show 99+% removal. (Table XIII).

(f) Fillers added as solid phosphates to make an 8-16-0 fertilizer ($8\% NO_3$, $16\% P_2O_5$).

Reliability of Emission Factors

Emission factor rankings are presented in Table XI. Emissions from every type source were not known but the major processing units were covered by actual data. These may not be typical of the entire industry. The available information does cover most areas that are known sources of particulate emission, and there was generally a very good duplication of results.

TABLE XI EMISSION FACTOR RANKINGS FOR AMMONIUM NITRATE PROCESSES

	Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total 0-40
Prilling Operation	10	8	5	23
Granulator Operation	10	8	5	23

APPENDIX

The unpublished source testing data [34] which was used to derive the emission factors are tabulated below. Emission factors were derived by averaging uncontrolled test data.

1. Prilling

TABLE XII PRILLING TOWER

Test(a)	Uncontrolled Particulate Emissions (NH_4NO_3) lbs/ton
1	0.75
2	0.825
3	0.99

(a) Each test consisted of velocity measurements and sampling at several representative locations in the effluent air stream.

TABLE XIII PRE DRYER

	Particulate Emissions NH_4NO_3), lbs/ton Product	
Test(a)	Uncontrolled(b)	Wet Cyclones
1	1.6	0.48
2	1.8	0.54

(a) Samples obtained by standard stack sampling techniques.

(b) Calculated figures, based upon an estimate of 70 percent efficiency for the wet cyclones.

	Particulate Emissions (NH_4NO_3), lbs/ton Product	
Test(a)	Uncontrolled(b)	Wet Cyclones
1	0.014	0.0042
2	0.019	0.0056

(a) Samples obtained by standard stack sampling techniques.

(b) Calculated figures, based upon an estimate of 70% efficiency for the wet cyclones.

TABLE XIV SECONDARY DRYER

Test[a]	Particulate Emissions (NH_4NO_3), lbs/ton Product	
	Uncontrolled [b]	Wet Cyclone
1	11.7	3.5
2	8.7	2.6

(a) Samples obtained by standard stack sampling techniques.

(b) Calculated figures, based upon an estimate of 70% efficiency for the wet cyclones.

TABLE XV WET SCREEN SCRUBBER (FOLLOWING CYCLONES ON DRYERS AND COOLERS)

Test[a]	Particulate Emissions (NH_4NO_3), lbs/ton Product
1	0.035

(a) Composite sample from many sections of equal area.

2. Granulation (8-16-0)

TABLE XVI GRANULATORS

	Emission as lbs/ton Product					
	Total Particulate		Nitrates (NO_3)		Ammonia (NH_3)	
Test[a]	No. Control[b]	Cyclone	No Control[b]	Cyclone	No Control[b,c]	Cyclone
1	0.28	0.083	0.077	.023	.44	.44
2	0.58	0.175	0.090	.027	.44	.44
3	-	-	0.093	.028	.57	.57

(a) Standard stack sampling techniques.

(b) Assume 70% cyclone efficiency.

(c) Assumption: No gaseous ammonia removed in dry cyclones.

TABLE XVII DRYER

	Emission as lbs/ton Product					
	Total Particulate		Nitrates (NO_3)		Ammonia	
Test (a)	No Control (b)	Cyclone	No Control	Cyclone	No Control (b,c)	Cyclone
1	3.60	1.08	0.90	.27	0.12	.12
2	2.50	0.75	0.93	.28	0.12	.12
3	3.90	1.17	1.97	.59	0.16	.16

(a) Standard stack sampling techniques.

(b) Assume 70% cyclone efficiency.

(b) Assumption: No gaseous ammonia removed in dry cyclones.

Table XVIII presents the additional emissions from the specific granular nitrate process where ammonium nitrate is granulated in the presence of superphospate filler to produce an 8-16-0 fertilizer.

TABLE XVIII MISCELLANEOUS EMISSIONS

	P_2O_5, lbs/ton Product	F^-, lbs/ton Product
Granulator	0.0021	0.0012
Dryer	0.030	0.033
Cooler	0.047	0.044

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particulate loading during the demonstration test was 258 ng/J (0.6 lb/10^6 Btu).

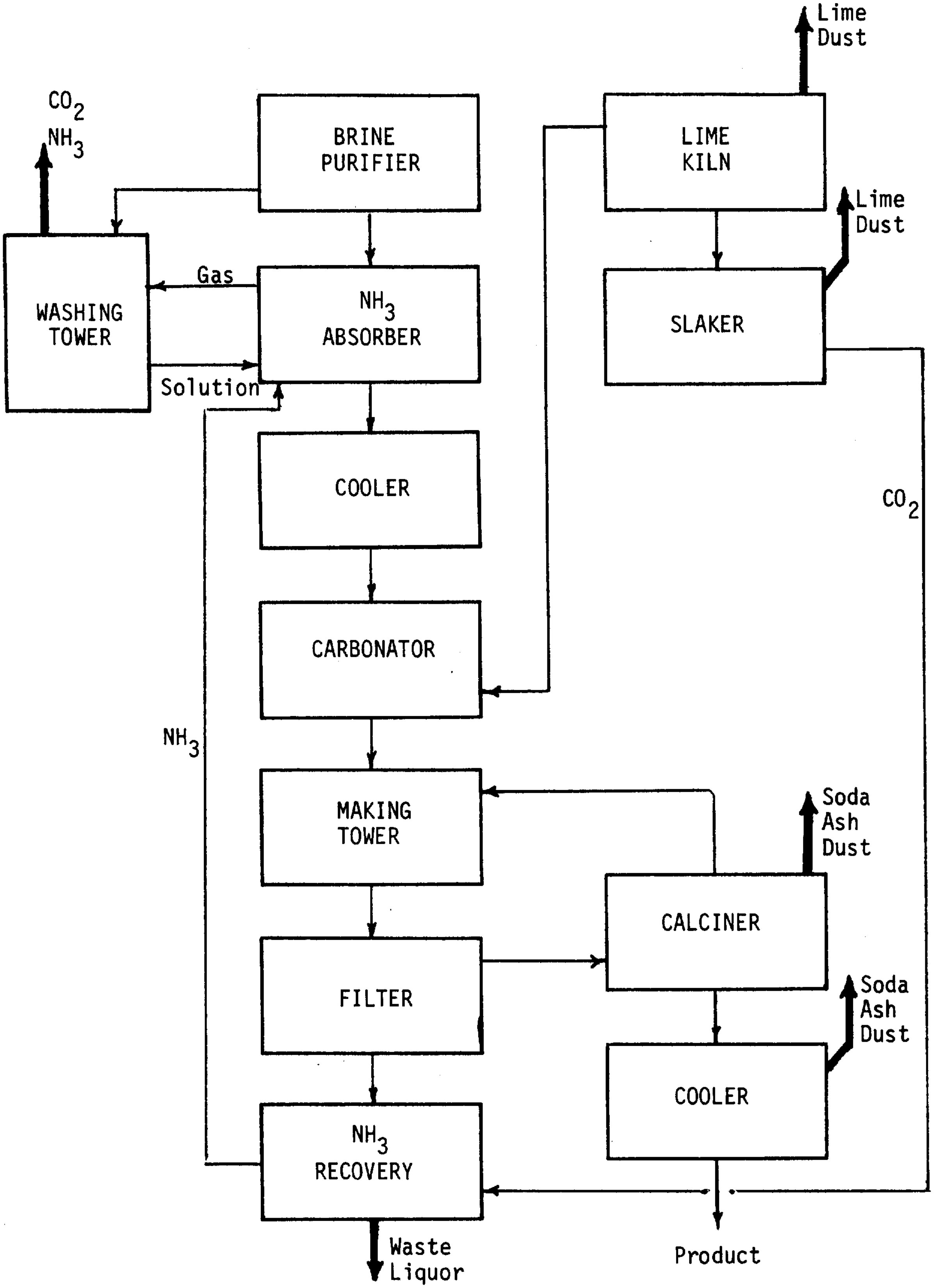

FIGURE 13. Simplified Flow Chart of the Ammonia-Soda (Solvay) Process (Emission points are shown by heavy arrows)

Lime Kiln Reactions	$(CaCO_3 \xrightarrow{heat} CaO + CO_2)$ $(C + O_2 \xrightarrow{burn} CO_2)$
Lime Slaking	$CaO + H_2O \longrightarrow Ca(OH)_2$(Milk of lime)
Ammoniation and Carbonation	$NaCl(brine) + NH_3 + CO_2 + H_2O \longrightarrow NaHCO_3 + NH_4Cl$
Bicarbonate Calcination	$2\ NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$
Ammonia Recovery	$2\ NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + 2H_2O + CaCl_2$

Limestone is converted to unslaked lime and carbon dioxide in vertical or rotary kilns. The carbon dioxide is reacted with ammonia and water to form ammonium bicarbonate, which is in turn reacted with sodium chloride to form sodium bicarbonate and ammonium chloride. Sodium bicarbonate crystallizes and is filtered from solution. The filter cake is calcined in rotary kilns where for every mol of sodium carbonate (soda ash) formed, a mol of carbon dioxide gas is evolved. The carbon dioxide is returned to process. The ammonium chloride solution which was separated from sodium bicarbonate by filtration is further processed to recover unreacted ammonia. Slaked lime reacted with ammonium chloride in solution forms ammonia and waste calcium chloride. Ammonia driven off by heat reacts with additional carbon dioxide in solution to form mol ammonium bicarbonate. Unreacted ammonia and carbon dioxide gas are sent to a washing tower in which most of the gas is absorbed by the incoming brine for further use in the process. Unabsorbed gases are vented.

Table XX lists the process points of emissions and the corresponding type of emission. Limestone unloading is also a minor source; emissions can usually be controlled by wetting down before unloading.[41]

Table XX. Sources and Emissions, Solvay Process Plants

Source	Emissions
Limestone Unloading	Limestone Dust
Lime Kiln	Lime Dust
Air Classifiers	Soda Ash Dust
Product Conveying	Soda Ash Dust
Bulk Loading	Soda Ash Dust
Washing Tower	Saturated NH_3 + CO_2 Gases

FACTORS AFFECTING EMISSIONS

Losses from the lime kiln are typical of that operation. The dust emission from vertical lime kilns is generally lower than that from rotary kilns. This is due to the larger size of the limestone being fed, lower gas velocities, and relative absence of abrasion of the charge when passing through the kiln. The dust generated by the rotary kiln ranges from 5 to 15 percent by weight of the lime produced.[42] This dust escapes at the discharge of the kiln. Local ventilation hoods which discharge to wet scrubbers serving rotary kilns have operated efficiently. A reverse-jet tabular type baghouse has been reported to result in additional recovery of lime dust over the use of collection system consisting of a centrifugal collector, settling chamber, and scrubber. A well-designed kiln hood on a vertical kiln can reduce the emissions significantly.

Sodium carbonate formed in the calcining of sodium bicarbonate is a low density material (light ash). There is considerable demand for a denser material (dense ash) which is made by mixing water with the light ash and redrying. Product is screened to the desired size range and then additional dust is removed by air classification.[41] The dust is collected by dry cyclones, which may be followed by a washer or preferably bag filters. The same control devices may also be used to recover dust emission from product conveying and loading operations.[41] The volume of particulate emissions will depend on whether light or dense soda ash is being produced.

Almost one-half ton of ammonia is continuously being absorbed, recovered and reabsorbed for every ton of soda ash produced. Final absorption before venting of inert gases and carbon dioxide is carried out in the washing tower where brine is used to recover ammonia and part of the CO_2. About 2 pounds NH_3/ton soda ash is not recovered in the washing tower and must be vented.[8]

Various fuels may be used for firing the lime kiln, calciner and dryer. Emission factors for these fuels will depend on the fuel used and its ash and sulfur content.

EMISSIONS

Emission factors are shown in Table XXI. No data are available on particulate emission from the various steps in processing dry soda ash and estimates from a material balance are not accurate because sodium carbonate losses in the waste liquor are high compared with atmospheric losses.[47]

Ammonia emission factors are based on reported makeup requirements less ammonia losses in the waste liquor, which are small.[47,48]

TABLE XXI. UNCONTROLLED EMISSION FACTORS FOR SODA Ash Manufacturing by Solvay Process

Operation	lb/ton Soda Ash Particulates	 NH_3	Ref.
Vertical Lime Kiln	3.6-13.8	--	42,48
Rotary Lime Kiln	113-339	--	42,48
Washing Tower	--	1.3-3.1[(a)]	47,48

(a) After in process control.

Table XXII gives the efficiencies of various control devices used in these operations.

TABLE XXII. REPORTED CONTROL DEVICES FOR LIME PLANT OPERATIONS [42]

Operations	Control Method	Collection Efficiency, %
Limestone unloading	Water sprayer	No data
Vertical kiln	Hood and bag filter	No data
Rotary kiln	Glass bag filter	99.99
Rotary kiln	4 stage cyclonic scrubber	97.5 - 99.7
Rotary kiln	High efficiency cycloner	70.0
Rotary kiln	Venturi scrubber	96.97
Rotary kiln	Impingement scrubber	97.5

RELIABILITY OF EMISSION FACTORS

Rankings based on the various factors which affect the accuracy of emission factors are presented in Table XXII. Data for lime dust emissions are quite reliable for non-captive plants but higher than would be expected for soda ash operations because in the latter case some in-process recovery is obtained by the utilization of the carbon dioxide emissions. Ammonia factors are based entirely on process data and engineering analysis.

Table XXIII. SODA ASH EMISSION FACTOR RANKING

	Emission Data 0-20	Process Data 0-10	Engineering Analysis 0-10	Total
Particulate	12	6	5	23
Ammonia	0	8	5	13

APPENDIX

1. Vertical Lime Kiln

Typical emission factor is 3.2 - 12.3 lbs. $\frac{\text{particulates}}{\text{ton lime}}$ [42]

1.125 ton lime (3.2 to 12.3) = 3.6 to 13.8 $\frac{\text{lbs particulates}}{\text{ton soda ash}}$ [48]

2. Rotary Lime Kiln

Typical emissions will range from 5 to 15% of weight of lime produced.[42]

1.125 ton lime x 2000(0.05 to 0.15) = 113 to 339 $\frac{\text{lbs. particulates}}{\text{ton soda ash}}$ [48]

3. Washing Tower

Amonnia makeup is in the range 1.5 - 3.3 $\frac{\text{lbs.}}{\text{tons soda}}$ [48]

Ammonia lost in waste liquor is about 0.2 $\frac{\text{lbs.}}{\text{tons soda ash}}$ [47]

46 percent was found for residual oil, and nearly 100 percent for distillate oil.[35] For coal-fired units the fuel nitrogen conversion varies depending on the combustion conditions present with the particular boiler and fuel (see Section 4.3).

3.2.1.4 Carbon Monoxide Emissions. The rate of CO emissions from boilers depends on the efficiency of the combustion of the fuel. By controlling the combustion process carefully, CO emissions can be minimized. The effects of combustion modifications for purpose of NO_x control on uncontrolled CO and HC emissions are discussed in Section 4.3 of this document.

3.2.1.5 Hydrocarbon Emissions. The rate of HC emission from boilers also depends on the combustion efficiency. Hydrocarbon emissions are minimized by use of proper combustion practices. Fuel type also affects HC emissions. Liquid and gaseous fuels have better mixing and firing characteristics than solid fuels, accounting in part for the lower hydrocarbon emissions for oil and natural gas-fired units than for comparable coal units.

3.2.1.6 Trace Element Emissions. Trace elements are found in fossil fuels, especially in coal and residual oil. Smaller concentrations of trace elements are also found in distillate oil, but virtually none are found in natural gas.

Trace elements can be classified according to the way they are emitted during the combustion process: (1) distributed between bottom ash and fly ash, (2) concentrated in fly ash, especially the fine particulate in the flue gas; or (3) as vapors. Trace elements that do not vaporize during fuel combustion are emitted in about equal concentration in bottom ash and fly ash particles. Those with lower boiling points, which vaporize during combustion, become concentrated in fly ash and are carried out by the flue gas. Some trace elements, such as mercury, are emitted through the stack into the atmosphere as vapors. Others, such as arsenic, cadmium, copper, lead, tin, and zinc, condense on fly ash particles and are emitted with them into the atmosphere.[36]