EPA 440/1-75/038
GROUP I, PHASE II

Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the

CALCIUM CARBIDE

Segment of the FERROALLOY MANUFACTURING Point Source Category

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
FEBRUARY 1975

DEVELOPMENT DOCUMENT

for

INTERIM FINAL EFFLUENT LIMITATIONS GUIDELINES

and

PROPOSED NEW SOURCE PERFORMANCE STANDARDS

for the

CALCIUM CARBIDE SEGMENT

of the

FERROALLOY MANUFACTURING POINT SOURCE CATEGORY

Russell E. Train
Administrator

James L. Agee
Assistant Administrator for
Water and Hazardous Materials

Allen Cywin
Director, Effluent Guidelines Division

Patricia W. Diercks
Project Officer, Ferroalloys

Elwood E. Martin
Project Officer, Inorganic Chemicals

February, 1975

Effluent Guidelines Division
Office of Water and Hazardous Materials
U.S. Environmental Protection Agency
Washington, D.C. 20460

ABSTRACT

For the purpose of establishing effluent limitations and standards of performance for the calcium carbide industry, the industry has been categorized on the basis of the types of furnaces, air pollution control equipment installed, raw materials and water uses. The categories are as follows:

I Covered Calcium Carbide Furnaces with Wet Air Pollution Control Devices; and
II Other Calcium Carbide Furnaces

Effluent limitations guidelines contained herein set forth the degree of effluent reduction attainable through the application of the best practicable control technology currently available (BPCTCA) and the degree of effluent reduction attainable through the application of the best available technology economically achievable (BATEA) which must be achieved by existing point sources by July 1, 1977 and July 1, 1983, respectively. The standards of performance for new sources contained herein set forth the degree of effluent reduction which is achievable through the application of the best available demonstrated control technology, processes, operating methods, or other alternatives.

Based upon best practicable technology currently available the covered furnace calcium carbide category may discharge a treated wet scrubber effluent. Based upon BPCTCA the other furnaces calcium carbide category is required to achieve no discharge of process wastewater.

Based on the application of best available technology economically achievable, the covered furnace category may discharge a treated wet scrubber effluent, while the other category is required to achieve no discharge of process wastewater.

The new source performance standards require no discharge of process wastewater for the other furnaces category, but allow a discharge of treated scrubber blowdown from the covered furnaces category.

Promulgated regulations for discharges from uncovered (open) calcium carbide furnaces appeared in the <u>Federal Register</u> on March 12, 1974 at page 9612 as part of the inorganic chemicals industry category. Although the subcategorization contained in this document does include open furnaces as part of the other carbide furnaces subcategory, the regulation to be published as part of the ferroalloys category will not duplicate the coverage of the inorganic chemicals regulation, but will be complementary to that regulation.

CONTENTS

FIGURES AND TABLES

SECTION I

CONCLUSIONS

For the purpose of establishing effluent limitations guidelines and standards of performance for the calcium carbide industry, the industry has been categorized on the basis of types of furnaces, air pollution control equipment, raw materials and water uses. The categories are as follows:

I Covered Calcium Carbide Furnaces with Wet Air Pollution Control Devices; and
II Other Calcium Carbide Furnaces

The effluent limitations guidelines for covered furnaces with wet scrubbers allow for a treated discharge of scrubber effluent with restrictions on suspended solids, pH and total cyanide. The proposed new source performance standards allow a discharge of treated blowdown from scrubber recirculation systems.

The proposed effluent limitations guidelines for other carbide furnaces is no discharge of process wastewater. 100 percent of this industry category is currently achieving this limitation. Covered furnaces which use evaporative coolers and dry bag collectors, or which have no air pollution control have no discharge of process wastewater.

SECTION II

RECOMMENDATIONS

It is recommended that the effluent limitations guidelines and new source performance standards be adopted as suggested herein for the calcium carbide industry. These suggested guidelines and performance standards have been developed on the basis of an intensive study of the industry, including plant surveys, and are believed to be reasonable and attainable from the standpoints of both engineering and economic feasibility.

It is recommended that the industry be encouraged to develop or adopt such pollution reduction methods as the recovery and reuse of collected airborne particulates for recycle to smelting operations and the use or sale of by-products. The development or adoption of better wastewater treatment controls and operating methods should also be encouraged.

The best practicable control technology currently available for existing point sources is as follows, by category:

Category I, Covered Furnaces with Wet Air Pollution Control Devices - physical/chemical treatment to reduce suspended solids and harmful pollutants; and

Category II, Other Furnaces - use of dry air pollution devices.

The effluent limitations to be achieved by July 1, 1977 are based on the pollution reduction attainable using those treatment technologies as presently practiced by the average of the best plants in the categories. The 30 day average effluent limitations corresponding to BPCTCA are as follows for category I:

pollutant parameter	kg/kkg (lb/1000 lb)
suspended solids	0.190
total cyanide	0.0028
pH	6.0-9.0

For category II, the effluent limitation is no discharge of process wastewater.

The best available technology economically achievable for existing point sources is as follows, by category:

I Scrubber effluent treated by physical/chemical treatment to reduce harmful pollutants followed by clarification and polish filtration to reduce suspended solids; and

II Same as BPCTCA

The effluent limitations to be achieved by July 1, 1983 are based on the pollution reduction attainable using those treatment technologies as presently practiced by the best plants in the categories along with transfer of technology from the inorganic chemicals industry. The 30 day average effluent limitations corresponding to BATEA are as follows for category I:

pollutant parameter	kg/kkg (lb/1000 lb)
suspended solids	0.11
total cyanide	0.0028
pH	6.0-9.0

For category II, the effluent limitation is no discharge of process wastewater.

The best available demonstrated control technology for new sources is as follows, by category:

I Recirculation of scrubber waste water, blowdown treated by physical/chemical treatment to reduce harmful pollutants followed by clarification and polish filtration to reduce suspended solids; and

II Same as BPCTCA

The new source performance standards are based upon the best available demonstrated control technology, process, operating methods, or other alternatives, which are applicable to new sources. For category I, the 30 day average effluent limitations for new sources are as follows:

pollutant parameter	kg/kkg (lb/1000 lb)
suspended solids	0.020
total cyanide	0.0005
pH	6.0-9.0

For category II, the effluent limitation is no discharge of process wastewater.

SECTION III

INTRODUCTION

PURPOSE AND AUTHORITY

The United States Environmental Protection Agency (EPA) is charged under the Federal Water Pollution Control Act Amendments of 1972 with establishing effluent limitations which must be achieved by point sources of discharge into the navigable waters of the United States.

Section 301(b) of the Act requires the achievement by not later than July 1, 1977, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best practicable control technology currently available as defined by the Administrator pursuant to Section 304(b) of the Act. Section 301(b) also requires the achievement by not later than July 1, 1983, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best available technology economically achievable which will result in reasonable further progress toward the national goal of eliminating the discharge of all pollutants, as determined in accordance with regulations issued by the Administrator pursuant to Section 304(b) to the Act. Section 306 of the Act requires the achievement by new sources of a Federal standard of performance providing for the control of the discharge of pollutants which reflects the greatest degree of effluent reduction which the Administrator determines to be achievable through the application of the best available demonstrated control technology, processes, operating methods, or other alternatives, including, where practicable, a standard permitting no discharge of pollutants. Section 304(b) of the Act requires the Administrator to publish within one year of enactment of the Act, regulations providing guidelines for effluent limitations setting forth the degree of effluent reduction attainable through the application of the best practicable control technology currently available and the degree of effluent reduction attainable through the application of the best control measures and practices achievable including treatment techniques, process and procedure innovations, operating methods and other alternatives. The regulations herein set forth effluent limitations guidelines pursuant to Section 304(b) of the Act.

Section 306 of the Act requires the Administrator, within one year after a category of sources is included in a list published pursuant to Section 306(b) (1) (A)) of the Act, to propose regulations establishing Federal standards of performances for new sources within such categories. The Administrator published in the Federal Register of January 16, 1973 (38 F.R. 1624), a list of 27 source categories. Publication of the list constituted announcement of the Administrator's intention of establishing, under Section 306, standards of performance applicable to new sources within the ferroalloy manufacturing point source category, which was included within the list published January 16, 1973.

SUMMARY OF METHODS USED FOR DEVELOPMENT OF EFFLUENT LIMITATION GUIDELINES AND STANDARDS OF PERFORMANCE

The Environmental Protection Agency has determined that a rigorous approach including plant surveys and verification testing is necessary for the promulgation of effluent standards from industrial sources. A systematic approach to the achievement of the required guidelines and standards includes the following:

a) categorization of the industry and determination of those industrial categories for which separate effluent limitations and standards need to be set;

b) characterization of the waste loads resulting from discharges within industrial categories;

c) identification of the range of control and treatment technology within each industrial category;

d) identification of those plants having the best technology currently available (exemplary plants); and

e) generation of supporting verification data for the exemplary plants including actual sampling of plant effluents by field teams.

The culmination of these activities is the development of the guidelines and standards based on the best practicable current technology and best available technology.

Categorization and Waste Load Characterization

The effluent limitations and standards of performance proposed herein were developed in the following manner. The point source category was first categorized for the purpose of determining whether separate limitations and standards are appropriate for different segments within a point source category. Such categorization was based upon type of furnace, air pollution devices, treatment technology and other factors. The raw waste characteristics for each category were then identified. This included an analysis of (1) the source and volume of water used in the process employed and the sources of waste and waste waters in the plant; and (2) the constituents of all waste waters including harmful constituents and other constituents which result in degradation of the receiving water. The constituents of waste waters which should be subject to effluent limitations and standards of performance were identified.

Treatment and Control Technologies

The full range of control and treatment technologies existing within each category was identified. This included an identification of each control and treatment technology, including both in-plant and end-of-process technologies, which are existent or capable of being designed for each category. It also included an identification of the amount of constituents and the characteristics of pollutants resulting from the application of each of the treatment and control technologies. The problems, limitations and reliability of each treatment and control technology were also identified. In addition, the non-water quality environmental impact, such as the effects of the application of such technologies upon other pollution problems, including air, solid waste, noise and radiation were also identified. The energy requirements of each of the control and treatment technologies were identified as well as the cost of the application of such technologies.

Data Base

Cost information contained in this report was obtained directly from industry during plant visits, from engineering firms and equipment suppliers, and from the literature.

The information obtained has been used to develop capital, operating and overall costs for each treatment and control method. Costs have been put on a consistent industrial calculation basis of ten year straight line depreciation plus allowance for interest at six percent per year (pollution abatement tax free money) and inclusion of allowance for insurance and taxes for an overall fixed cost amortization of fifteen percent per year. This cost data plus the specific information obtained from plant visits was then used for cost effectiveness estimates in Section VIII and wherever else costs are mentioned in this report.

The data for identification and analyses were derived from a number of sources. These sources included EPA research information, published literature, qualified technical consultation, on-site visits and interviews at plants throughout the U.S., interviews and meetings with trade associations, and interviews and meetings with regional offices of the EPA. All references used in developing the guidelines for effluent limitations and standards of performance for new sources reported herein are included in Section XIII of this report.

Exemplary Plant Selection

The following exemplary plant selection criteria were developed and used for the selection of exemplary plants.

a) Discharge effluent quantities

Plants with low effluent quantities or the ultimate of no discharge of process waste water pollutants were preferred. This minimal discharge may be due to reuse of water, raw material recovery and recycling, or to use of evaporation. The significant parameter was minimal waste added to effluent streams per weight of product manufactured. The amount of wastes considered here were those added to waters taken into the plant and then discharged.

b) Effluent contaminant level

Preferred plants were those with lowest effluent contaminant concentrations and lowest total quantity of waste discharge per unit of product.

c) Water management practices

Use of good management practices such as water re-use, planning and in-plant water segregation were considered.

d) Land utilization

The efficiency of land use was considered.

e) Air pollution and solid waste control

Exemplary plants must possess overall effective air and solid waste pollution control where relevant in addition to water pollution control technology. Care was taken to insure that all plants chosen have minimal discharges into the environment and that exemplary sites are not those which are exchanging one form of pollution for another of the same or greater magnitude.

f) Effluent treatment methods and their effectiveness

Plants selected have in use the best currently available treatment methods, operating controls, and operational reliability. Treatment methods considered included basic process modifications which significantly reduce effluent loads as well as conventional treatment methods.

g) Plant facilities

All plants chosen as exemplary had all the facilities normally associated with the production of the specific material in question. Typical facilities generally were plants which have all their normal process steps carried out on-site.

h) Geographic location

Factors which were considered include plants operating in close proximity to sensitive vegetation or in densely populated areas. Other factors such as land availability, rainfall, and differences in state and local standards were also considered.

i) Raw materials

Differences in raw material purities were given strong consideration in cases where the amounts of wastes are strongly influenced by the purity of raw materials used.

General Description of Calcium Carbide Manufacturing

There is only one process used in the United States for the manufacture of calcium carbide. This process involves the thermal reduction of calcium oxide (lime) and coke in a submerged arc electric furnace. The calcium oxide and dried coke are conveyed to a mix-house where they are weighed and blended. After the batch has been formulated it is moved by conveyor to the hoppers above the furnace, where it flows by gravity through chutes to the furnace.

Electricity is passed through carbon electrodes extending below the surface of the charge so that a thermal reduction zone lies in the center of the charge. The molten calcium carbide from the carbon reduction of lime accumulates at the base of the electrodes in the furnace. The molten alloy is periodically removed through the tap-hole to drain the material from the hearth of the furnace. The calcium carbide is cooled in air in chill cars or hoppers, then crushed, screened and packaged for shipment. Quality control tests are made on batches to determine the volume of acetylene produced by a known quantity of calcium carbide.

The basic design of the submerged-arc furnace for the production of calcium carbide is the same throughout the industry with the notable exception of open versus covered furnaces. In the open furnaces the carbon monoxide reaction gas is combusted with air at the surface of the charge, and the large quantities of gases flow into a hood built above the furnace. The gases are discharged through a stack to the atmosphere or are passed through air pollution control devices such as a baghouse or venturi scrubber. Due to the open configuration, the parts above the furnace charge are exposed to the radiant heat of the furnace and the hot furnace gases. These components, along with the electrical transformers are cooled through the use of non-contact cooling water. Figure 1 shows a schematic of an open furnace.

Covered furnaces have water cooled covers extending over the top of the furnace crucible with openings for the electrodes and gas removal dusts. The openings around the electrodes are generally used for charging raw materials. In covered furnaces, raw materials such as metallurgical coke and lime chunks are used that do not tend to bridge or block the flow of gas so that furnace eruptions are minimized.

The crucible of the submerged-arc furnace consists of a metal shell adequately supported on foundations with provisions for cooling the bottom of the steel shell. The bottom interior of the steel shell is lined with two or more layers of carbon blocks and tightly sealed with a carbon compound packed between the joints. The interior walls of the furnace shell are lined with refractory or carbon brick. One or more tap-holes are provided through the shell. In some cases, provisions are made for the furnace to rotate slowly. Submerged-arc furnaces generally operate continuously except for periods of power interruption or mechanical breakdown of components. Operating time varies from 90 to 98 percent, with 95 percent a good average.

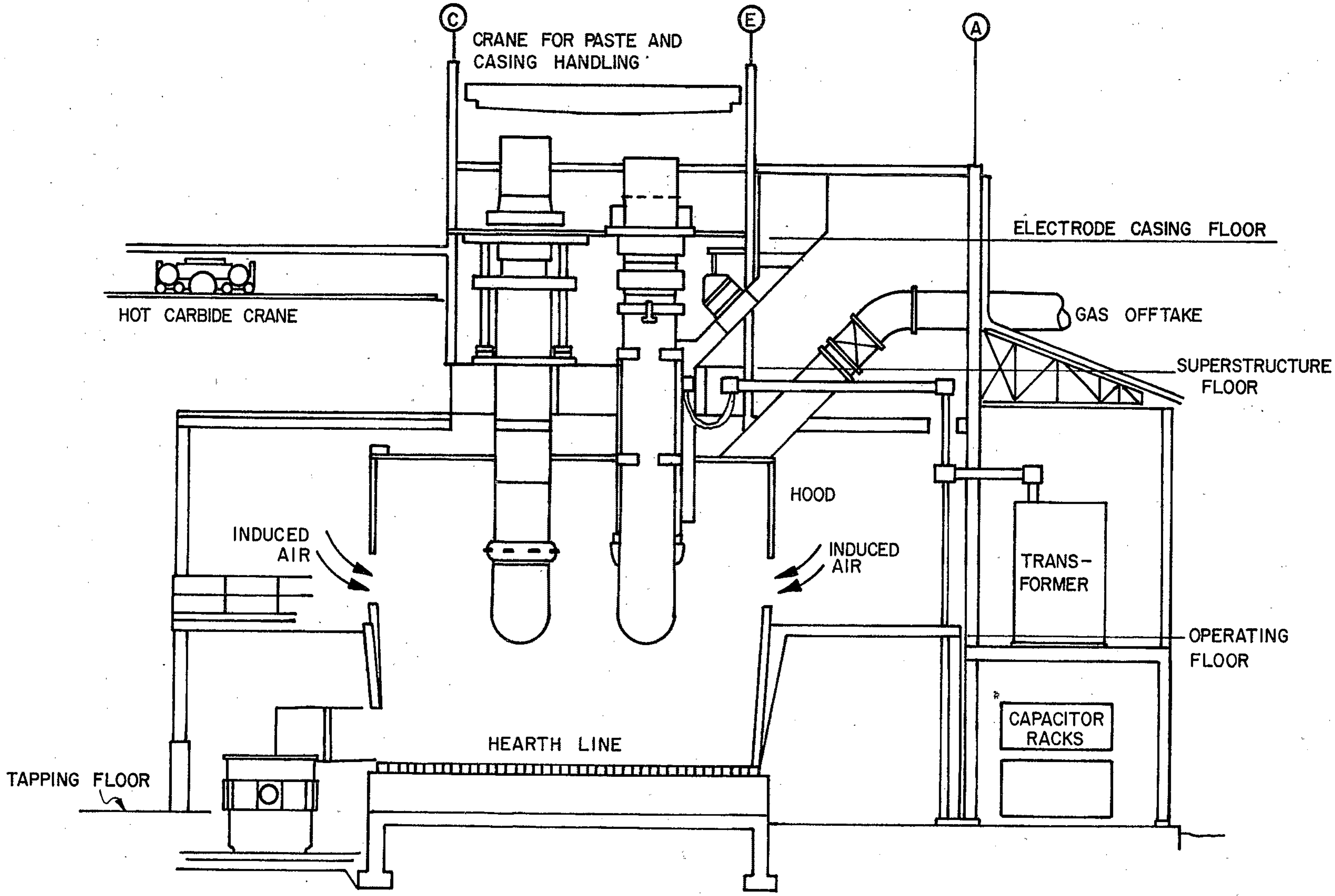

FIGURE I
CROSS SECTION OF OPEN FURNACE

Although furnaces may be changed from production of one product to another, such as from calcium carbide to ferro-alloys, this almost always entails rearrangement of electrode spacing and involves different power loads and voltage requirements.

In the production of calcium carbide by the electric-arc furnace process, the only source of process water pollutants is the use of wet air pollution control devices such as scrubbers. The sources of air pollution are thus of importance. Particulates are emitted from coke drying, crushing, grinding and sizing and furnace operations. The particulate emissions from the drying, crushing and sizing operations are generally handled in dry collectors such as baghouses or cyclones. Dry collection is also used for the fumes from the furnace tapping and emissions from the electrode areas in a covered furnace. Wet scrubbers may be used to handle the gases from the furnace reaction.

Since the emissions from the furnace have a major impact upon the potential for water pollution in those plants using wet air pollution control devices, some discussion of such emissions is appropriate. The submerged-arc furnace utilizes carbon reduction of lime, and continuously produces large quantities of hot carbon monoxide. The CO gas venting from the top of the furnace carries fumes from high-temperature regions of the furnace and entrains the finer sized constituents of the mix.

In an open furnace, all CO and other combustibles in the furnace gas burn with induced air at the top of the charge, resulting in a large volume of high-temperature gas. In a covered furnace, most or all of the CO and other gases are withdrawn from the furnace without combustion.

Except for ejected mix particles from the furnace the fume size is generally below two microns. Grain loadings and flowrates are dependent upon the furnace type and hooding. Open submerged-arc furnaces have high flowrates and moderate grain loadings, while closed furnaces have moderate flowrates and generally high grain loadings.

The quantity of emissions from calcium carbide submerged-arc furnaces will vary up to several times the normal emission level over a period of one to three percent of the operating time due to major furnace interruptions and, to a lesser extent, because of normal interruptions. The quantity and type of emissions are also dependent on the presence of fines in the feed. Fine materials promote bridging and non-uniform descent of the charge which may cause gas channels to develop. The collapse of a bridge causes a momentary burst of gases. A porous charge will promote uniform gas distribution and decrease bridging. For some locations economics dictates the use of raw materials with more fines or with more volatile matter than desirable. An example of this is the operation of an open furnace when using petroleum coke as a raw material which has a greater amount of fines than metallurgical coke. Use of an open furnace, however, allows the charge to be 'stoked', thereby breaking up bridges.

SECTION IV

INDUSTRY CATEGORIZATION

INTRODUCTION

The development of effluent limitations guidelines and recommended standards of performance for new sources for a particular industry must give consideration to whether the industry can be treated as a whole in the establishment of uniform and equitable guidelines or whether there are sufficient differences within the industry to justify its division into categories. For the calcium carbide segment of the ferroalloy industry, the following categorization is believed to yield the least number of groups having significant differences in water pollution control and treatment.

The proposed categories are:

I - Covered Calcium Carbide Electric Furnaces With Wet Air Pollution Control Devices; and
II - Other Calcium Carbide Electric Furnaces

In developing the above categorization, the following factors were considered as a possible basis:

1) Production Processes
2) Furnace Types
   a) Open
   b) Covered
3) Raw Materials
4) Product Produced
5) Size & Age of Facilities
6) Wastewater Constituents
7) Water Uses
8) Air Pollution Control Equipment
9) Treatment Technology

Production Processes

Since there is only one production process used for the production of calcium carbide, this is not a basis for categorization.

Furnace Types

The types of electric furnaces used to produce calcium carbide were found to provide a basis for categorization in conjunction with raw materials, water uses and air pollution control equipment. The differences between open and covered furnaces are significant as they relate to the raw waste loads from the process, particularly the presence or absence of carbon monoxide in the furnace gases. The furnace gas volumes from the two types of furnaces may vary by a factor of 20 and the water used for wet air pollution control devices varies significantly in terms of hydraulic load due to the differences in gas volumes. In general, covered furnace operations tend to recover and utilize the carbon monoxide in the furnace gas, while open furnace operations burn the carbon monoxide to carbon dioxide in the process.

Raw Materials

The types of raw materials used to produce calcium carbide were found to provide a basis for categorization in conjunction with furnace types, water uses and air pollution control equipment. The basic differences in raw materials are the use of metallurgical coke versus petroleum coke. The choice of these two raw materials is based partly on economics and geographical location. The plants located in the western part of the U.S. use petroleum coke while those in the east and midwest use metallurgical coke. The use of a specific type of coke dictates the type of furnace used for the process. When petroleum coke is used, the production of calcium carbide is carried out in an open furnace due to the small sized particles characteristic of the raw material. The use of an open furnace is necessary due to the amount of particle emissions and eruptions from the furnace charge. On the other hand, all of the furnaces using metallurgical coke are covered and, therefore, must handle the problem of carbon monoxide in the furnace off-gas.

Product Produced

Since only one product is produced, there is no basis for further categorization. However, it should be pointed out that it is possible to produce other products such as ferroalloys in a furnace now producing calcium carbide, but the production processes are not readily interchangeable and a furnace will not be used one week for calcium carbide, and the next for ferroalloy production. The furnace is always committed to the production of one product at a time. It is not felt that the possible convertability of a carbide furnace to a ferroalloy furnace provides an adequate basis for categorization.

Size and Age of Facilities

The size and age of facilities does not provide a basis for categorization. Plant ages range from 5 to 46 years with sizes ranging from 20,000 to 150,000 tons per year. This type of range does not provide adequate justification for categorization.

Waste Water Constituents

The waste water constituents do not provide an independent basis for categorization. With the exception of non-contact cooling water, the only water used in the process is for wet air pollution devices. Suspended solids are the largest single constituent of the process wastewater, and result from removal of particulates from the furnace gases. Cyanides are generated in significant concentrations only in covered furnaces. The wastewater constituents are due to the differences between open and covered furnaces together with wet air pollution control devices and, therefore, are not a basis for categorization.

Water Uses

Water uses were found to provide a basis for categorization in conjunction with furnace types, raw materials and air pollution control equipment. Water is used in the process for two purposes -- cooling water and air pollution control devices. The cooling water is non-contact and can be once-through or recirculated via a cooling tower. Associated with this water there may be water used for water treatment regeneration and cooling tower blowdown. Water is also used for air pollution control equipment for wet scrubbing.

Air Pollution Control Equipment

Air pollution control is the primary pollution problem in this industry. The water pollution problem is created by solving air pollution problems with wet air pollution control devices. When a dry air pollution control system (such as a baghouse) is used, or when emissions are uncontrolled, there is no process waste water discharge. For this reason, the categorization selected is partially based upon type of air pollution equipment; i.e., wet or dry. Although the type of wet scrubber used for air pollution control was considered for further categorization, it was felt that the type of process furnace used would provide a better basis.

Treatment Technology

The only plant in the other carbide furnaces category which utilizes a wet air pollution control device is recycling all wastewater and therefore has no discharge. However, the only plant in the covered furnaces category presently using wet scrubbers does discharge treated scrubber wastewater.

SECTION V

WATER USE AND WASTE CHARACTERIZATION

INTRODUCTION

This section discusses the specific water uses in the calcium carbide industry, and the amounts of process waste materials contained in these waters. The process wastes are characterized as raw waste loads emanating from the manufacturing process and are given in terms of kilograms per metric ton of product (pounds per thousand pounds). The specific water uses and amounts are given in terms of liters per metric ton (gallons per ton) for each of the plants contacted in this study. The treatments used by the plants studied are specifically described and the amount and type of water-borne waste effluent after treatment is characterized.

SPECIFIC WATER USES

Water is used in calcium carbide plants for three principal purposes falling under three major characterization headings. The principal water uses are:

1) cooling -- non-contact cooling water

2) process water -- scrubber water

3) auxiliary processes water.

Non-contact cooling water is defined as that cooling water which does not come into direct contact with any raw material, intermediate product, by-product or product used in or resulting from the production process. Process water is defined as that water which, during the manufacturing process comes into direct contact with any raw material, intermediate product, by-product or product used in or resulting from the production process. Auxiliary processes water is defined as that used for processes necessary for production but not contacting the process materials. For example, water treatment regeneration is an auxiliary process.

The quantity of water usage for plants in this industry generally ranges from 50,000 to 100,000 liters per metric ton (12,000 to 24,000 gallons per ton). In general, the plants using large quantities of water use it for once-through cooling.

Non-Contact Cooling Water

The non-contact cooling water in the industry is generally of two types. The first type is recycled cooling water which is cooled by cooling towers or spray ponds. The second type is once-through cooling water whose source is generally a river, lake or tidal estuary, and this water is usually returned to the source from which it was taken. The quantity of cooling water for plants in this industry ranges from 40,000 to 80,000 liters per metric ton (9600 to 19,200 gallons per ton), or about 80% of the total water usage. Limitations for non-contact cooling water will be established for all industries in the future. At the present time, there is believed to be no excessive thermal load resulting from ferroalloys plants.

Air Scrubber and Contact Wash Water

This water comes under the heading of process water because it comes into direct contact with the raw material, reactants and product when used for wet scrubbing the furnace gases. The water usage varies in volume depending on the type of scrubber employed. A high energy venturi scrubber on an open furnace uses approximately 35,000 liters of water per metric ton (8,400 gallons per ton). A high energy venturi scrubber on a covered furnace uses as little as 1300 liters of water per metric ton (312 gallons per ton). Another form of contact wash water is that found in use in evaporative coolers, which are sometimes used to cool the burned furnace gas before entering a bag house. All of this water is consumed in evaporation and none would be discharged.

Miscellaneous Water Uses

These water uses vary widely among the plants with general usage for safety showers and eye wash stations, sanitary uses, and storm run-off. The resultant streams are either not contaminated or only slightly contaminated with wastes. The general practice is to discharge such streams without treatment except for sanitary waste. In instances where process residues collect where they can be washed away by storm waters, as for example dusts on the exterior of process buildings, storm run-off can constitute a contamination problem.

Auxiliary Processes Water

This water is used in moderate quantities by the typical plant for auxiliary operations such as ion exchange regenerants, and make-up water to cooling towers with a resultant cooling tower blowdown. The water effluents from these operations are generally low in quantity but highly concentrated in waste materials.

The waste effluent from recycled cooling water would be water treatment chemicals and the cooling tower blowdown which generally is discharged with the cooling water. The only waste effluent from once-through cooling water would be water treatment chemicals which are generally discharged with the cooling water. The cooling water tower blowdown may contain phosphates, nitrates, nitrites, sulfates, and chromates.

The water treatment chemicals may consist of alum, hydrated lime, or alkali metal ions (sodium or potassium) arising from ion exchange processes. Regeneration of the ion exchange units is generally accomplished with sodium chloride or sulfuric acid depending upon the type of unit employed. At the present time there is insufficient data upon which to base a regulation for auxiliary process water. Additionally, it is not directly related to production and is relatively small in quantity. Limitations for these discharges should be established on a case-by-case basis, with the weight of the proof on the permit applicant, at least until such time as a national standard is established.

PROCESS WASTE CHARACTERIZATION

In this section the following information is given:

- -- a short description of the differences in the processes at the plants studied and pertinent flow diagrams:
- -- raw waste load data
- -- water consumption data
- -- specific plant waste effluents found and the post-process treatments used to produce them;
- -- significant differences from plant data where found in verification measurements.

Plants Surveyed

The four producers of calcium carbide constituting 100 percent of the United States production of this chemical were contacted and plant visits were made to all five currently producing locations. The producers, locations, capacities and furnace type are listed in Table 1.

Process Description

Calcium oxide and dried metallurgical or petroleum coke are reacted in an electric-arc furnace. The calcium carbide product is tapped as a liquid from the furnace, then air cooled, crushed, screened, packaged and shipped. The process wastes are airborne dusts from the coke drier, screening and packaging operations and the furnace off-gases. The process reaction is:

$CaO + 3C \rightarrow CaC_2 + CO$

For every metric ton (1.1 short tons) of carbide produced, about 310 cubic meters (11,000 cubic feet) (15°C) of furnace gas is evolved; the gas analyzes 75-85 percent carbon monoxide, 5-12% hydrogen and the remainder is nitrogen, oxygen, carbon dioxide and methane.

There are two basic types of furnaces used for the process -- open and covered; the types of coke used, either metallurgical or petroleum, are dependent on furnace type. The open furnaces use petroleum coke for reaction and burn the furnace gases with air at the surface of the charge. These furnaces have a large volume of burned gases which must be handled by an air pollution control system. The covered furnaces use metallurgical coke for reaction and either burn the furnace off-gases in a combustion chamber to eliminate the carbon monoxide or scrub the gases and pipe the carbon monoxide to another operation to recover the fuel value. In all cases, particulate emissions are the major pollution problem from the coke drier, furnace and crushing-screening operations. The coke drying and crushing-screening operations dust emissions are handled by bag-filter collectors from which 15 to 50 percent of the dusts can be recycled and the remainder goes to land storage. Four of the five plants are currently operating in this fashion. The fifth plant uses dry collection on the crushing-screening operations and does not operate a coke drier at the present time. When coke drying is practiced at this plant, it is planned to combine the drier vent gases with furnace gases and control the emissions with the existing venturi scrubbers.

The major source of particulate emissions are from the furnace gases. The types of air pollution control equipment used for the furnace gases vary with the type of furnace and whether or not carbon monoxide is recovered. The types of air pollution control systems used in the calcium carbide plants are listed below. Figure 2 shows the process flow diagram for an open furnace operation, while Figures 3 and 4 show the process flow diagram for covered furnaces with and without wet scrubbers.

Types of Air Pollution Control Systems
Used On Calcium Carbide Furnace Stack Gases

1. Open furnaces with withdrawal and cleaning of burned gases

   Control device

   Wet scrubbers

   Cloth type filters (baghouse)

2. Covered furnaces with withdrawal and cleaning of unburned gases

   Control devices

   Wet scrubbers

3. Covered Furnaces with withdrawal and cleaning of burned gases

   Control devices

   Evaporative cooler and baghouse

Table 1. Calcium Carbide Producers

Location, Capacity, and Furnace Type

Producer	Location	Annual Capacity (thousands of tons)	Plant Type	Furnace Type
Airco, Inc. Airco Alloys & Carbide Div.	Louisville, Kentucky	150	CaC_2 only	Covered
	Calvert City, Kentucky[1]	325	Ferroalloy	Covered
Midwest Carbide Corp.	Keokuk, Iowa	30	CaC_2 only	Covered
	Pryor, Oklahoma	50	CaC_2 only	Open
Pacific Carbide & Alloys Co.	Portland, Oregon[2]	20	CaC_2 only	Open
Union Carbide Corp. Ferroalloys Div.	Ashtabula, Ohio	228	Ferroalloy	Covered

[1] Calcium carbide production at Calvert City was discontinued early in 1973, but industry sources indicate that production will be resumed within the next several years.

[2] Calcium carbide production will be expanded at this plant within the next several years.

Sources: Oil Paint and Drug Reporter, December 15, 1969, February 22, 1971, and Industry Sources.

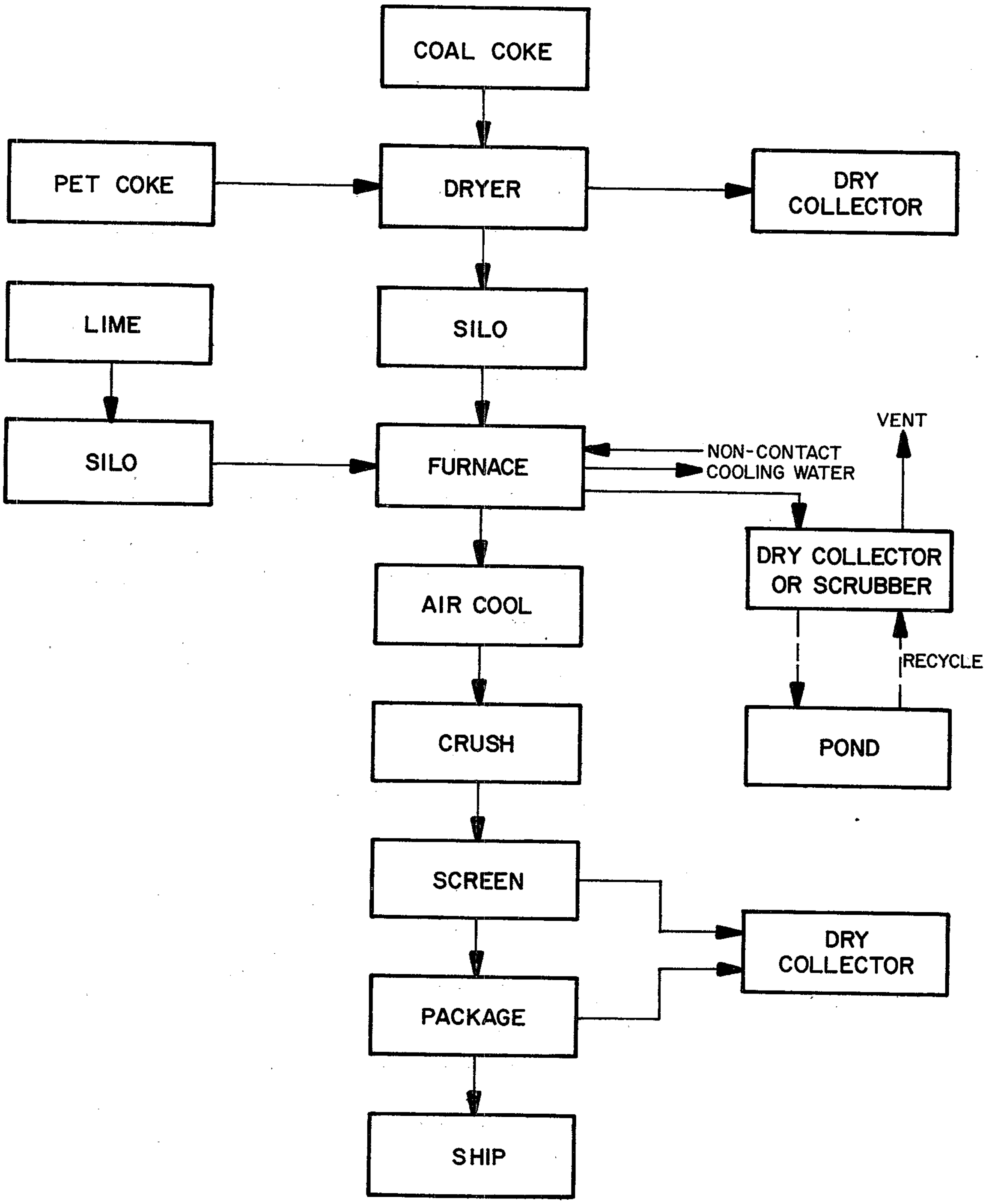

FIGURE 2

OPEN FURNACE CALCIUM CARBIDE PROCESS FLOW DIAGRAM

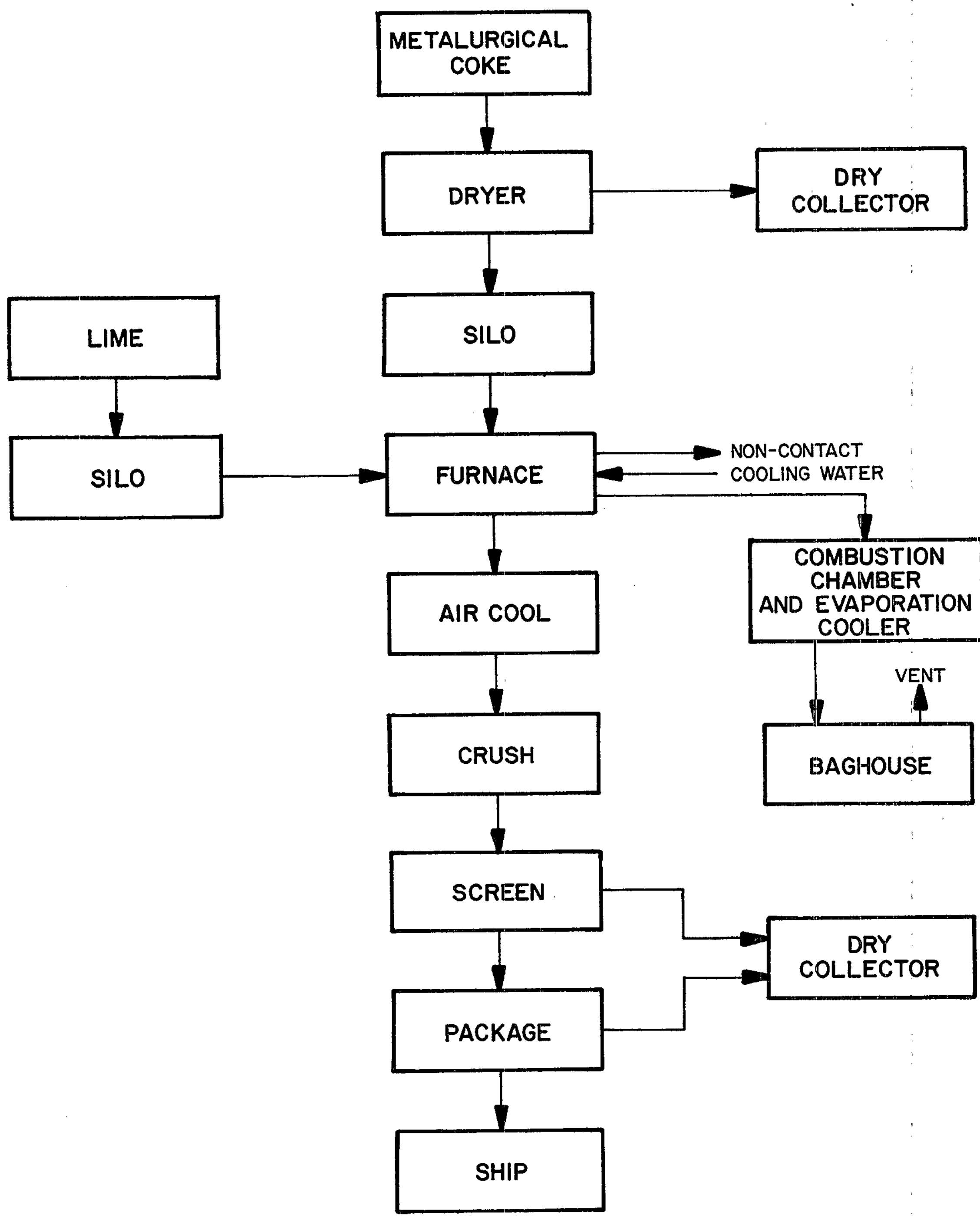

FIGURE 3

COVERED FURNACE CALCIUM CARBIDE PROCESS FLOW DIAGRAM WITH DRY COLLECTION DEVICES

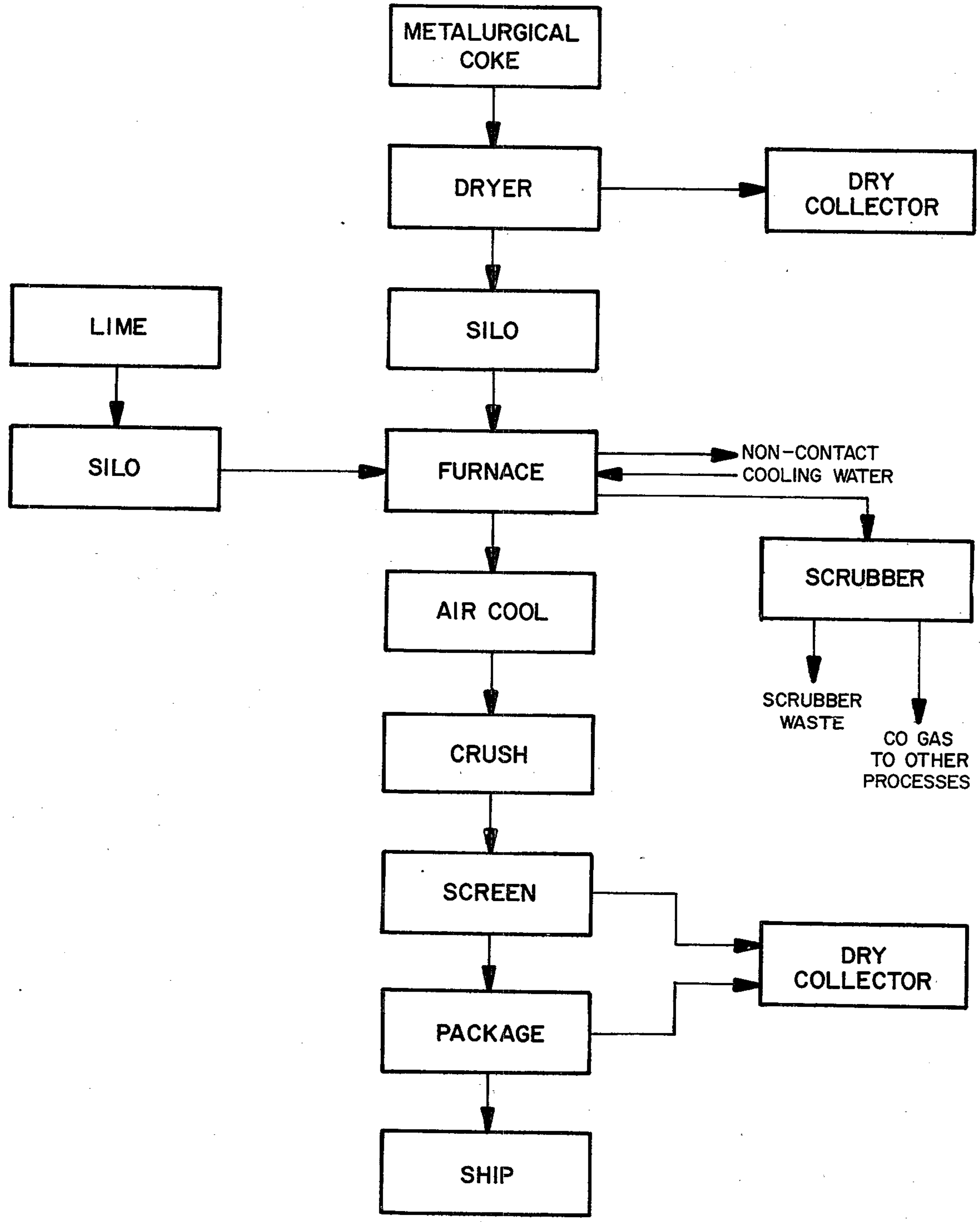

FIGURE 4

COVERED FURNACE CALCIUM CARBIDE PROCESS FLOW DIAGRAM WITH WET AIR POLLUTION DEVICE

Raw Waste Loads

The main process reaction generates no by-product raw waste material. Process raw wastes are generated by the coke drier, furnace gas scrubbing, and packaging operations. The average values are given for the two open furnace plants below:

waste material	plant 454 kg/kkg (lb/1000 lb)	plant 455 kg/kkg (lb/1000 lb)
coke dust	none	50
furnace stack dust	135	85
packing dust	unknown	10
hydrated lime and coke	112.5	---

Plant 454 does not operate a coke drier but does landfill some coke spillage along with off grade calcium carbide after "airslaking" to hydrated lime. Plant 455 recycles up to 50 percent of the fines to the furnace and landfills the remainder.

The average raw waste loads from the covered furnace plants are given below:

waste material	plant 451 kg/kkg (lb/1000 lb)	plant 452 kg/kkg (lb/1000 lb)	plant 453 kg/kkg (lb/1000 lb)
coke dust	20	30.3	3.9
furnace stack dust	23	28	37.5
packing dust	unknown	unknown	31.
cyanide (total)	0.203	none	none

The packing dusts from these three plants are recycled to the operation and go out with the product.

Wet Scrubber Raw Waste Loads

Samples of scrubber raw wastes were analyzed by the contractor with the following results:

constituent	plant 451 concentration (mg/l)	calculated kg/kkg (lb/1000 lb)
TSS	3750	28.2
TDS	302	2.3
Cyanide (total)	27	0.203
Iron	14.2	0.11
Silica (SiO_2)	2.9	0.02
Calcium	397	2.98
Flow (gal/ton)	1800	
	plant 454	
TSS	4740	166.
TDS	2640	92.5
Cyanide	--	---
Iron	22.7	0.80
Silica (SiO_2)	0.24	0.0084
Calcium	2570	90.1
Flow (gal/ton)	8400	

Air Pollution Control Equipment

The following is a summary of the types of air pollution equipment found in use or planned for furnace off-gas emission control. The use of wet scrubbers is more prevalent with covered furnaces than with open.

Open Furnace Operation

furnace gas air pollution equipment	plant 455	plant 454
dry bag filters	installed and operating	none in use but considering for future
venturi high energy wet scrubber	none	presently in use

Covered Furnace Operation

furnace gas air pollution equipment	plant 451	plant 452	plant 453
venturi wet scrubber	none	planned installation 1974	none
evaporative cooler and dry bag filter	none	presently in use	planned installation 1974
disintegrator scrubbers	presently in use	none	none

Plant 453 currently vents and flares all furnace gases.

The Airco plant at Calvert City, Kentucky which is currently not operating, is a covered furnace operation which presently uses no air pollution control equipment, but Airco sources indicate that a venturi wet scrubber installation is projected for that plant when it comes back on stream.

The venturi high energy scrubbers have been the most recent wet scrubbers to be installed in the calcium carbide plants. A high energy venturi scrubber on an open furnace uses approximately 35,000 liters of water per metric ton (8400 gallons per ton). The same installation on a covered furnace uses as little as 1300 liters of water per metric ton (312 gallons per ton). Most venturi designs allow recirculation of scrubbing solutions, such that the water consumption is reduced to that evaporated plus that contained in the blowdown of the concentrated solids stream.

A disintegrator type of scrubber is used by one of the plants surveyed. This type of scrubber has the advantage of producing only a slight pressure head in the off-gas line, but capacity limitations and large water and power consumption make it uneconomical for most new furnace installations.

The use of an evaporative cooler and dry bag collector has definite advantages in that there is no waste water effluent from the system. The water sprays used to cool the gas are totally evaporated. The main disadvantage of this system is that the carbon monoxide must be burned before entering the system.

Plant Water Use

Water is used in these plants for non-contact cooling and gas scrubbing. The various modes of water consumption at the plants are:

Open Furnace Operation

consumption	liters/metric ton (gal/ton) plant 454	plant 455
non-contact cooling	41,700(10,000)	49,900(12,000)
scrubbers	35,000(8,400)	none

Plant 455 recirculates water through a cooling tower, while plant 454 uses once through cooling water.

Covered Furnace Operation

consumption	plant 451	plant 452	plant 453
non-contact cooling	40,000(9,600)	54,600(13,100)	80,000(19,000)
scrubbers	7,500(1,800)		

Plants 452 and 453 recirculate water through a cooling tower, while plant 451 uses cooling water for other operations in the complex before discharging. Plant 452 is currently installing a wet scrubber which will have a planned water consumption of 1300 liters per metric ton (312 gal/ton).

Waste Water Treatment

Plant 455 has no process waste water due to dry collection methods. Plant 454 totally recycles the venturi scrubber water through two settling ponds. This system has been in operation for over two years. Plant 452 has no process waste water because it is presently cleaning only burned gases by dry methods. Plant 452 is currently installing a wet scrubber and is planning to treat the blowdown from the recycled scrubber water by clarification and neutralization. Plant 453 has no scrubber waste water, since no gases are cleaned. Plant 451 is a ferroalloy complex which treats its waste water in a treatment system using chlorination, clarification, and neutralization.

Plant Effluents

Plants 452, 453, 454, and 455 presently do not discharge process waste water. They do discharge non-contact cooling water and water treatment streams. Plant 454, using total recycle of the venturi scrubber water, indicated some discharge of pond water during periods of unusual rain fall. Plant 452 is planning to discharge the blowdown of its proposed scrubber along with cooling tower blowdown to a municipal sewer.

The average combined discharges of plant 451 (ferroalloy complex) are given as follows:

waste water	concentration (mg/l)		
constituents	outfall 001	outfall 002	intake
TSS	24	25	29
TDS	255	324	247
BOD	none	none	none
COD	15	18	12
pH	8.3	8.3	8.3
cyanide	0.065	0.005	0.005
phenols	0.100	0.050	0.050
hardness (total)	139	147	130
chloride	47	90	36
fluoride	0.70	0.52	0.22
sulfate	26	45	22
iron	2.331	2.565	1.863
copper	0.090	0.090	0.090
chromium	0.030	0.030	0.030
manganese	0.176	0.166	0.166
arsenic	0.010	0.010	0.010
mercury	0.001	0.001	0.001
lead	0.005	0.005	0.005

These discharges, on a gross basis, are from a combined series of plant operations and are presently diluted with cooling water prior to discharge.

SECTION VI

SELECTION OF POLLUTANT PARAMETERS

INTRODUCTION

The wastewater constituents of significance for this segment of the industry are based upon those parameters which have been identified in the untreated wastes from each category of this study. The waste water constituents are further divided into those that have been selected as pollutants of significance, with the rationale for their selection, and those that are not deemed significant, with the rationale for their rejection.

SIGNIFICANCE AND RATIONALE FOR SELECTION OF POLLUTION PARAMETERS

The basis for selection of the significant pollutant parameters was:

1) toxicity to humans, animals, fish and aquatic organisms;
2) substances causing dissolved oxygen depletion in streams;
3) soluble constituents that result in undesirable tastes and odors in water supplies;
4) substances that result in eutrophication and stimulate undesirable algae growth;
5) substances that produce unsightly conditions in receiving water; and
6) substances that result in sludge deposits in streams.

Selected as pollutant parameters were:
- Cyanide;
- Total Suspended Solids; and
- pH.

Cyanide$^-$, Total

Cyanides in water derive their toxicity primarily from undissolved hydrogen cyanide (HCN) rather than from the cyanide ion (CN^-). HCN dissociates in water into H^+ and CN^- in a pH-dependent reaction. At a pH of 7 or below, less than 1 percent of the cyanide is present as CN^-; at a pH of 8, 6.7 percent; at a pH of 9, 42 percent; and at a pH of 10, 87 percent of the cyanide is dissociated. The toxicity of cyanides is also increased by increases in temperature and reductions in oxygen tensions. A temperature rise of 10°C produced a two- to threefold increase in the rate of the lethal action of cyanide.

Cyanide has been shown to be poisonous to humans, and amounts over 18 ppm can have adverse effects. A single dose of about 50-60 mg is reported to be fatal.

Trout and other aquatic organisms are extremely sensitive to cyanide. Amounts as small as .1 part per million can kill them. Certain metals, such as nickel, may complex with cyanide to reduce lethality, especially at higher pH values, but zinc and cadmium cyanide complexes are exceedingly toxic.

When fish are poisoned by cyanide, the gills become considerably brighter in color than those of normal fish, owing to the inhibition by cyanide of the oxidase responsible for oxygen transfer from the blood to the tissues.

pH

The term pH is a logarithmic expression of the concentration of hydrogen ions. At a pH of 7, the hydrogen and hydroxyl ion concentrations are essentially equal and the water is neutral. Lower pH values indicate acidity while higher values indicate alkalinity.

Waters with a pH below 6.0 are corrosive to water works structures, distribution lines, and household plumbing fixtures and can thus add such constituents to drinking water as iron, copper, zinc, cadmium and lead. The hydrogen ion concentration can affect the "taste" of the water. At a low pH water tastes "sour". The bactericidal effect of chlorine is weakened as the pH increases, and it is advantageous to keep the pH close to 7. This is very significant for providing safe drinking water.

Extremes of pH or rapid pH changes can exert stress conditions or kill aquatic life outright. Dead fish, associated algal blooms, and foul stenches are aesthetic liabilities of any waterway. Even moderate changes from "acceptable" criteria limits of pH are deleterious to some species. The relative toxicity to aquatic life of many materials is increased by changes in the water pH. Metallocyanide complexes can increase a thousand-fold in toxicity with a drop of 1.5 pH units. Ammonia is more lethal with a higher pH.

The lacrimal fluid of the human eye has a pH of approximately 7.0 and a deviation of 0.1 pH unit from the norm may result in eye irritation for the swimmer. Appreciable irritation will cause severe pain.

Solids, Suspended

Suspended solids include both organic and inorganic materials. The inorganic components include sand, silt, and clay. The organic fraction includes such materials as grease, oil, tar, animal and vegetable fats, various fibers, sawdust, hair, and various materials from sewers. These solids may settle out rapidly and bottom deposits are often a mixture of both organic and inorganic solids. They adversely affect fisheries by covering the bottom of the stream or lake with a blanket of material that destroys the fish-food bottom fauna or the spawning ground of fish. Deposits containing organic materials may deplete bottom oxygen supplies and produce hydrogen sulfide, carbon dioxide, methane, and other noxious gases.

In raw water sources for domestic use, state and regional agencies generally specify that suspended solids in streams shall not be present in sufficient concentration to be objectionable or to interfere with normal treatment processes. Suspended solids in water may interfere with many industrial processes, and cause foaming in boilers, or encrustations on equipment exposed to water, especially as the temperature rises. Suspended solids are undesirable in water for textile industries; paper and pulp; beverages; dairy products; laundries; dyeing; photography; cooling systems, and power plants. Suspended particles also serve as a transport mechanism for pesticides and other substances which are readily sorbed into or onto clay particles.

Solids may be suspended in water for a time, and then settle to the bed of the stream or lake. These settleable solids discharged with man's wastes may be inert, slowly biodegradable materials, or rapidly decomposable substances. While in suspension, they increase the turbidity of the water, reduce light penetration and impair the photosynthetic activity of aquatic plants.

Solids in suspension are aesthetically displeasing. When they settle to form sludge deposits on the stream or lake bed, they are often much more damaging to the life in water, and they retain the capacity to displease the senses. Solids, when transformed to sludge deposits, may do a variety of damaging things, including blanketing the stream or lake bed and thereby destroying the living spaces for those benthic organisms that would otherwise occupy the habitat. When of an organic and therefore decomposable nature, solids use a portion or all of the dissolved oxygen available in the area. Organic materials also serve as a seemingly inexhaustible food source for sludgeworms and associated organisms.

SIGNIFICANCE AND RATIONALE FOR REJECTION OF POLLUTION PARAMETERS

A number of pollution parameters besides those selected were considered, but had to be rejected for one or several of the following reasons:

1) insufficient data on degradation of water quality;
2) not usually present in quantities sufficient to cause water quality degradation;
3) treatment does not "practicably" reduce the parameter; and
4) simultaneous reduction is achieved with another parameter which is limited.

Acidity/Alkalinity

Acidity and/or alkalinity, reported as calcium carbonate, are quantitative measurements of the amount of neutralization to be required in the receiving stream. There does not appear to be any need for their determination in effluent wastewaters where the pH is between 6.0 and 9.0.

$Calcium^{2+}$

Although calcium does exist in some quantity in the wastewaters, there is no treatment to practicably reduce it.

Phosphates

Phosphates contribute to eutrophication in receiving bodies of water. However, they were not found in quantities sufficient to cause water quality degradation.

$Potassium^{+}$

Although potassium does exist in quantity in the wastewaters, there is no treatment to practicably reduce it.

Silica

Silica may be present in the wastewaters but it is simultaneously reduced with another parameter which is limited.

Sodium$^+$

Although sodium does exist in quantity in the wastewaters, there is no treatment to practicably reduce it.

Solids, Dissolved

The total dissolved solids is a gross measure of the amount of soluble pollutants in the wastewater. It is an important parameter in drinking water supplies and water used for irrigation. A total dissolved solids content of less than 500 mg/l is considered desirable. From the standpoint of quantity discharged, TDS could have been considered for selection as a pollutant parameter. However, energy requirements (especially for evaporation) and solid waste disposal costs are usually so high as to preclude limiting dissolved solids at this time.

Temperature

Temperature is a sensitive indicator of unusual thermal loads where waste heat is involved in the process. Excess thermal load has not been and is not expected to be a significant problem in scrubber wastewater.

SECTION VII

CONTROL AND TREATMENT TECHNOLOGY

INTRODUCTION

The majority of water-borne wastes from the calcium carbide industry are suspended solids, primarily calcium hydroxide, calcium oxide and coke. The other component of the industry's water-borne waste load is dissolved solids, mainly as low valued materials such as calcium chloride, but containing small quantities of hazardous substances such as cyanides.

Specific Treatment and Control Practices

Cooling water, either once-through or recycled by means of a cooling tower, should be relatively free of wastes. Any contaminants present would come from leaks or recycle buildups (cooling tower) which are handled as ancillary water blowdown. In either event, cooling waste contributions are small and treatment should not normally be needed.

Process and ancillary water-borne wastes usually require treatment. The type, degree and costs involved will depend upon specific circumstances unique for each chemical.

Suspended Solids Removal

Suspended solids occur as part of the water-borne waste load, as a result of air pollution abatement.

Many of the suspended materials are relatively inert. Most of the suspended solids removed prior to wastewater discharge eventually wind up as land-disposed solid waste.

Settling Ponds

Settling ponds are the major mechanism used for reducing the suspended solids content of water waste streams. Their performance depends primarily on the settling characteristics of the solids suspended, the flow rate through the pond and the pond size. Settling ponds can be used over a wide range of suspended solids levels. Often a series of ponds is used, with the first ponds collecting the heavy load of easily settleable material and the following ones providing final polishing to reach a desired final suspended solids level. Sludge removal and disposal from settling ponds is often a major solid waste problem. Rarely is there any suspended solids treatment after the final settling pond. In most cases, the suspended solids level from the final pond ranges from 10 to 30 mg/liter, but for some, the values range up to 100 mg/liter.

Clarifiers and Thickeners

An alternate method of removing suspended solids is through the use of clarifiers and thickeners. Commercially, these units are listed as clarifiers or thickeners depending on whether they are light or heavy duty. Clarifiers and thickeners are essentially tanks with internal baffles, compartments, sweeps and other directing and segregating mechanisms to provide efficient concentration and removal of suspended solids in one effluent stream and clarified liquid in the other. Usually the stream containing most of the suspended solids is either sent to a second thickening vessel or sent directly to a centrifuge or filter for further concentration to sludge or cake solids. Another alternative is to send the slurry stream to settling ponds.

Filtration

Filtration is the most versatile method for removal of waterborne suspended solids, being used for applications ranging from dewatering of sludges to removal of the last traces of suspended solids to give clear filtrates.

Filtration is accomplished by passing the wastewater stream through solids -- retaining screens, cloths, or particulates such as sand, gravel, coal or diatomaceous earth using gravity, pressure or vacuum as the driving force.

Filtration equipment is of various designs, including plate-and-frame, cartridge and candle, leaf, vacuum rotary, and sand or mixed media beds. All of these types are currently used in the treatment of water-borne wastes in the inorganic chemical industry.

Centrifuging

When the force of gravity is not sufficient to separate solids and liquids to the desired degree or in the desired time, centrifugal force can be utilized. Although there are many types of centrifuges, most industrial units can be broken down into major categories -- solid bowl and perforated bowl. The solid bowl centrifuge consists of a rapidly rotating bowl into which the waste stream is introduced. Centrifugal action of the spinning bowl separates the solids from the liquid phase and the two are removed separately. The perforated bowl centrifuge has holes in the bowl through which the liquid escapes by centrifugal force. The solids are retained inside the bowl and removed either continuously or in batch fashion.

Centrifuges are not widely used for ferroalloys or inorganic chemical waste streams when compared to settling ponds, thickeners, or filters.

Coagulation

Suspended solids may settle slowly or not at all due to their small particle size and electrical charges. Addition of a flocculant or coagulant neutralizes these charges, promotes coagulation of particles and gives faster settling rates and improved separation.

Coagulants, such as alum, ferric chloride and polymeric electrolytes, also aid in the settling of other suspended solids that may be present.

Dissolved Materials Treatment

Treatment for dissolved materials consists of either modifying or removing the undesired materials. Modification techniques include chemical treatment such as neutralization and oxidation-reduction reactions. Cyanides are examples of dissolved materials modified in this way. Removal of dissolved solids is accomplished by methods such as chemical precipitation, ion exchange, carbon adsorption, reverse osmosis and evaporation.

Chemical Treatment

Chemical treatments for abatement of water-borne wastes are widespread. Included in this overall category are such important subdivisions as neutralization, pH control, oxidation-reduction reactions, coagulation, and precipitation.

Neutralization

Water-borne wastes may be either acidic or alkaline. Before disposal to surface water or other medium, this acidity or alkalinity needs to be controlled. The most common method is to treat acidic streams with alkaline materials such as limestone, lime, soda ash, or sodium hydroxide. Alkaline streams are treated with acids such as sulfuric. Whenever possible, advantage is taken of the availability of acidic waste streams to neutralize basic waste streams and vice versa. Neutralization often produces suspended solids which must be removed prior to waste water disposal.

Oxidation

Cyanides

The two most common methods of treating cyanides are: (1) single or two-staged alkaline chlorination and (2) hypochlorite oxidation.

Alkaline Chlorination

Stage 1 (fast)

$$NaCN + Cl_2 + 2NaOH \overset{11.5\ pH}{=} NaCNO + 2NaCl + H_2O$$

Stage 2 (slow)

$$2NaCNO + 3Cl_2 + 4NaOH \overset{7.5\ to\ 9.0\ pH}{=} N_2 + 2CO_2 + 6NaCl + 2H_2O$$

The stage 1 cyanates are stable and less toxic than cyanides. Stage 2 completes the destruction to nitrogen and carbon dioxide, but considerably more chlorine and caustic are required for the overall 2-stage process than for the single-stage oxidation to cyanate. The reaction is also slower.

Hypochlorite Oxidation

$$2NaCN + Ca(OCl)_2 = 2NaCNO + CaCl_2$$

$$2NaCN + 2NaOCl = 2NaCNO + 2NaCl$$

Either calcium or sodium hypochlorite can be used depending on economics and availability. For small plants or small cyanide wastewater loads, the recently developed electrical hypochlorite generators may be useful.

Both alkaline chlorination and hypochlorite treatments normally reduce oxidizable cyanide to essentially zero concentration.

Ozone has also been used for oxidation of cyanides. Other methods include boiling and peroxide decomposition.

Complex cyanides are more resistant to oxidation or removal than simple cyanides. Soluble complex cyanides may often be removed by chemical precipitation with iron salts (such as ferrous sulfate) or other heavy metal ions (zinc or cadmium).

Evaporation

The industrial use of evaporation in treating wastewater has been minimal. As the cost of pure water has increased in portions of the United States and the world, however, it has become increasingly attractive to follow this approach.

Almost always, the treatment of waste water streams by evaporation has utilized the principle of multi-effects to reduce the amount of steam or energy required. Thus, the theoretical limitation of carrying out the separation of a solute from its solvent is the minimum amount of work necessary to effect the particular change, that is, the free energy change involved. A process can be made to operate with a real energy consumption not greatly exceeding this value. The greater the concentration of soluble salts, the greater is the free energy change for separation, but, even for concentrated solutions, the value is much lower than the 550 kg-cal per kilogram value to evaporate water. Multi-effect evaporators use the heat content of the evaporated vapor stream from each preceding stage to efficiently (at low temperature difference) evaporate more vapor at the succeeding stages. Thus, the work available is used in a nearly reversible manner, and a low energy requirement results. However, a large capital investment in heat transfer surface and pumps is required.

Drying

After evaporative techniques have concentrated the dissolved solids to high levels, the residual water content must still be removed for either recovery, sale or disposal. Water content will range from virtually zero up to 90 percent by weight. Gas or oil fired dryers, steam heated drum dryers or other final moisture-removing equipment can be used for this purpose. Since this drying operation is a common one in the production of inorganic chemicals, technology is well known and developed. Costs are mainly those for fuel or steam.

Containment

Rainwater Runoff

Rainwater runoff of suspended or dissolved wastes is of concern for a number of plants. Ore piles, ore residues, and solid wastes as well as airborne wastes which settle as dusts and mists on buildings and grounds are contributors.

Pond Containment

Unlined ponds are the most common treatment facility used by the ferroalloys and inorganic chemicals industries. Ponds are often used in closed loop or zero discharge systems. In dry climates the ponds may serve as disposal basins.

Containment failures of ponds occur because they are unlined, or they are improperly constructed for containment in times of heavy rainfall.

Unlined ponds may give good effluent control, if dug in impervious clay areas, or poor control, if in porous, sandy soil. The porous ponds will allow effluent to diffuse into the surrounding earth and water streams. Plastic pond linings are being increasingly used to avoid this problem.

In times of heavy rainfall, many ponds overflow and much of the pond content is released into either the surrounding countryside or, more likely, into the nearest body of water. Good effluent control may be gained by a number of methods, including:

1) Pond and diking designed to take any anticipated rainfall -- smaller and deeper ponds used where rainfall is heavy.

2) Construct ponds so that drainage from the surrounding area does not inundate the pond and overwhelm it.

3) Substitution of smaller volume (and covered) treatment tanks, coagulators or clarifiers to reduce rainfall influx and leakage problems.

Disposal Practices

Disposal of the water-borne wastes from manufacturing represents the final control exercised by the waste producer. A number of options are available, some at zero or low cost, others at high cost.

Low-cost options include discharge to surface water -- river, lake, bay or ocean -- and where applicable, land disposal by running effluent out on land and letting it soak in or evaporate.

At somewhat higher costs, wastes may be disposed of into the municipal sanitary system or an industrial waste treatment plant. Treatment and reuse of the waste stream can also be practiced. In dry climates unlined evaporation ponds, if allowed, would involve moderate costs.

High-cost disposal systems include lined evaporation ponds, deep well disposal, and ocean barging. Such methods are used for wastes which cannot be disposed of otherwise. These wastes contain strong acids or alkalies, harmful substances, and/or high dissolved solids content.

Unlined Evaporation Ponds

Two requirements must be met for an unlined evaporation pond to be successfully utilized. First it must be located in an area in which unlined ponds are allowed, and secondly, the rainfall in that area must not exceed the evaporation rate. This second requirement eliminates most of the heavily industrialized areas. For the low rainfall areas, evaporation ponds are feasible with definite restrictions. Ponds must be large in area for surface exposure. The volume of water evaporation per year can be determined by the following formula:

$$\text{Volume} = 0.00274 \times D \times \text{area}$$

Where D = difference between meters of water evaporated per year and meters of rainfall per year.

Evaporation of large amounts of waste water requires large ponds. The availability and costs of sufficient land place another possible restriction on this approach.

Lined Evaporation Ponds

The lined evaporation ponds now required in some sections of the country have the same characteristics as developed for the unlined ponds -- large acreage requirements and a favorable evaporation rate to rainfall balance. They are significantly higher in cost than an unlined pond. Reduction of the evaporation load prior to its ponding is a significant advantage. For this reason, plus the short supply and high cost of water in much of the southwestern

United States, distillation and membrane processes are beginning to be used -- either alone or in conjunction with evaporation ponds -- in these regions.

Municipal Sewers

Although the water-borne wastes from some plants were treated on-site, the study revealed one plant that plans to dispose of their wastes to a municipal sewer system.

SECTION VIII

COST, ENERGY AND NON-WATER QUALITY ASPECTS

COST AND REDUCTION BENEFITS OF TREATMENT AND CONTROL TECHNOLOGIES

INTRODUCTION

In general, plant size and age have only a nominal effect in influencing the waste effluents and the costs for their treatment and disposal. Although large plants and complexes have lower treatment costs per unit of product when the same methods are used, the small plants can often use municipal sewers, land seepage, commercial disposal and other methods not available or economic to the larger producers. Plant age indirectly influences treatment and disposal costs through the effects of isolation and control of wastes and space limitations and cost. If treatment and disposal space is available and waste streams are isolable then age usually makes little difference.

Removal of dissolved solids may be expensive. The disposal of soluble solids once they have been removed from the wastewater is another problem. New plants have more options in solving these problems economically than do existing plants. New source facilities with heavy dissolved solids effluents and/or heavy solid waste loads may avoid costly wastewater treatment by geographical location. A favorable balance of climatic evaporation to rainfall eases these problems. Land storage or landfill space should be available for solids disposal.

New plants being built can avoid major future waste abatement costs by inclusion of: (1) piping, trenches, sewers, sumps, and other isolation facilities to keep leaks, spills and process water separate from cooling and sanitary water, (2) efficient reuse, recycling and recovery of all possible raw materials and by-products, (3) closed cycle water utilization whenever possible. Closed cycle operation eliminates all water-borne wastes to surface water.

COST DATA

Cost information contained in this report was obtained directly from industry, from engineering firms, equipment suppliers, government sources, and available literature. Whenever possible, costs are based on actual industrial installations or engineering estimates for projected facilities as supplied by contributing companies. In the absence of such information, cost estimates have been developed from either plant-supplied costs for similar waste treatment installations or general cost estimates for treatment technology. Costs were calculated for every plant surveyed. In the treatment cost table the values of invested capital and annual costs given are the maximum for the industry category, and are incremental costs. Thus, the maximum investment for a plant to attain Level C would be a total of $14.09 per metric ton. Land costs are not included due to the variability with location.

Costs have been uniformly calculated based on 10 percent straight line depreciation. There is an additional amount of interest at 6 percent of the depreciated value per year (pollution-abatement tax-free money). These plus the costs of insurance and taxes yield a total overall annualized fixed cost of 15 percent per year.

All costs have been adjusted to 1971 values and are quoted as such unless otherwise noted.

Definition of Levels of Treatment and Control Cost Development

Costs are developed for several levels of applied technology:

Minimum (or Basic) Level - practices followed by all of the involved plants. Usually money for this treatment level has already been spent (in the case of capital investment) or is being spent (in the case of operating and overall costs).

B and C Levels - Successively greater degrees of treatment with respect to critical pollutant parameters.

Treatment and Disposal Rationales Applied to Cost Developments

The following treatment rationales are employed in the cost development:

1) All non-contact cooling water is exempted from treatment (and treatment costs) provided that no harmful pollutants are introduced.

2) Water treatment, cooling tower and boiler blowdown discharges are not treated provided they contain no harmful pollutants.

3) Disposal considerations are covered in cost development, including evaporation ponds, land spoilage and solid wastes handling.

Wastewater Treatment and Control Costs

Category I Covered Furnaces with Wet Air Pollution Control Devices

The wastes from the production of calcium carbide in covered furnaces are primarily furnace dusts and carbon monoxide gas. In order to recover the carbon monoxide for fuel value, several plants are now using or are planning to install wet scrubbers. One plant currently operates an evaporative cooler and dry bag collector, but also flares some of the furnace gases. This plant will incur additional costs for the installation of piping and clarification equipment to treat the blowdown from a new wet scrubber installation. This plant will also incur costs for discharge to a municipal treatment system. This plant is going to wet scrubbing to eliminate an air pollution problem and recover furnace gas fuel value. A second plant operates disintegrator scrubbers with once through water usage and treats the scrubber waste in a total plant treatment system.

A cost summary for this category is given in Table 2. Level A costs are estimated to be $0.18 per metric ton of calcium carbide for investment. $0.07 has already been spent by one plant and $0.03 per metric ton is projected to be spent in 1974 by another plant. Annual costs are estimated to be $0.06 per metric ton. Capital and operating costs for plant 451 were estimated on a prorated basis for the total complex treatment system apportioned to the percentage of calcium carbide furnaces in the complex. Level B costs for additional treatment of scrubber wastewater by polish filtration are estimated to be $0.88 per metric ton for investment and $0.26 per metric ton for annual costs. With a selling price of $110 per metric ton, the maximum investment cost is 0.8 percent of the selling price while the annual cost is 0.2 percent. Level C costs for recycle of the scrubber wastewaters are estimated to be $13.03 per metric ton for investment and $3.90 per metric ton for annual costs.

Category II Other Furnaces

The wastes from the production of calcium carbide in open furnaces are primarily furnace dusts. One plant in the category collects all dusts in a dry bag-filter system and, therefore, has no process water effluent. A second plant in this category operates a venturi scrubber to treat the furnace dusts. The water from the scrubber is sent to two settling ponds and totally recycled to the scrubber. A third plant currently flares all gases from covered furnaces, but is installing an evaporative cooler and dry bag collector. This category has 100 percent of the plants presently operating at zero discharge of pollutants in process waste water, and therefore, there is no additional cost to meet a no discharge limitation for the entire category.

Solid Waste

For those waste materials considered to be non-hazardous where land disposal is the choice for disposal, practices similar to proper sanitary landfill technology may be followed. The principles set forth in the EPA's Land Disposal of Solid Wastes Guidelines (CFR Title 40, Chapter 1; Part 241) may be used as guidance for acceptable land disposal techniques.

For those waste materials considered to be hazardous, disposal will require special precautions. In order to ensure long-term protection of public health and the environment, special preparation and pretreatment may be required prior to disposal. If land disposal is to be practiced, these sites must not allow movement of pollutants such as fluoride and radium-226 to either ground or surface water. Sites should be selected that have natural soil and geological conditions to prevent such contamination or, if such conditions do not exist, artificial means (e.g., liners) must be provided to ensure long-term protection of the environment from hazardous materials. Where appropriate, the location of solid hazardous materials disposal sites should be permanently recorded in the appropriate office of the legal jurisdiction in which the site is located.

TABLE 2

WATER EFFLUENT TREATMENT COSTS
FERROALLOY INDUSTRY
CALCIUM CARBIDE
Covered Furnaces with Wet Air Pollution Control Devices

Treatment or Control Technologies:	A	B	C
Investment ($/annual metric ton)	0.18	0.88	13.03*
Annual Costs: ($/metric ton)			
Capital	0.01	0.05	0.65
Depreciation	0.02	0.09	1.30
Operation & Maintenance	0.02	0.09	1.30
Energy & Power	0.01	0.03	0.65
TOTAL	0.06	0.26	3.90*
Effluent Quality kg/kkg (lb/1000 lb)			
Parameters			
Suspended Solids	0.03-0.19	0.11 max	0.020 max
Cyanide	0.0028	0.0028	0.0005
pH	8.3-9.0	8.3-9.0	8.3-9.0

Level Descriptions:

Level A--Treatment of wet scrubbing effluent by chlorination, clarification and neutralization.
Level B--Same as Level A plus polish filtration.
Level C--Recycle of scrubber water.

*Costs include replacement of scrubbers where necessary for recycle.

SECTION IX

EFFLUENT REDUCTION ATTAINABLE THROUGH THE APPLICATION OF THE BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE

The effluent limitations which must be achieved by July 1, 1977, are based on the degree of effluent reduction attainable through the application of the best practicable control technology currently available. For the calcium carbide industry, this level of technology was based on the average of the best existing performance by plants of various sizes and ages, within each of the industry categories. Each category will be treated separately for the recommendation of effluent limitations guidelines and standards of performance.

Best practicable control technology currently available emphasizes treatment facilities at the end of a manufacturing process but also includes the control technology within the process itself when it is considered to be normal practice within an industry. Examples of waste management techniques which are considered normal practice are:

a) manufacturing process controls;

b) recycle and alternative uses of water; and

c) recovery and/or reuse of wastewater constituents.

Consideration was also given to:

a) The total cost of application of technology in relation to the effluent reduction benefits to be achieved from such applications;

b) The size and age of equipment and facilities involved;

c) The process employed;

d) The engineering aspects of the application of various types of control techniques;

e) Process changes; and

f) Non-water quality environmental impact (including energy requirements).

The following is a discussion of the best practicable control technology currently available for each of the categories, and the proposed limitations on the pollutants in their effluents.

General Water Guidelines

Process water is defined as any water contacting the reactants, intermediate products, by-products or products of a process including contact cooling water. All values of the guidelines and limitations presented below for total suspended solids (TSS) and harmful pollutants are expressed as a maximum 30 day average in units of kilograms of pollutant per metric ton (pounds of pollutant per thousand pounds) of product. The daily maximum limitation is double the 30 day average, except for pH. All process water effluents are limited to the pH range of 6.0 to 9.0 unless otherwise specified.

Based on the application of best practicable technology currently available, the recommendations for the discharge of cooling water are as follows.

An allowed discharge of all non-contact cooling waters provided that the following conditions are met:

a) Thermal pollution be in accordance with standards to be set by EPA policies.

b) All non-contact cooling waters should be monitored to detect leaks from the process. Provisions should be made for treatment to the standards established for process waste water discharges prior to release.

c) No untreated process waters be added to the cooling waters prior to discharge.

The above non-contact cooling water recommendations should be considered as interim, since this type of water plus blowdown from water treatment, boilers and cooling towers will be regulated by EPA at a later date as a separate category.

PROCESS WASTE WATER GUIDELINES AND LIMITATIONS

Category I - Covered Calcium Carbide Furnaces With Wet Air Pollution Control Devices

Based upon the information contained in Sections III through VIII, a determination has been made that the degree of effluent reduction attainable through the application of the best practicable control technology currently available is:

Effluent Characteristic	Effluent Limitation kg/kkg (lb/1000 lb)
TSS	0.190
cyanide (total)	0.0028
pH	6.0-9.0

The above limitations were based on an average process wastewater discharge of 7,500 liters per metric ton (1800 gallons per ton).

Identification of BPCTCA

Best practicable control technology currently available for the manufacture of calcium carbide in covered furnaces with scrubbers is treatment of all scrubber wastes by chlorine oxidation to reduce total cyanide followed by clarification to reduce suspended solids and neutralization to pH 6 to 9.

To implement this technology at plants not already using the recommended control techniques would require the installation of chlorine treatment systems, clarifiers or settling ponds, and acid neutralization plus the necessary piping and pumps.

Reason for Selection

The only plant presently discharging process wastewater is using this technology.

Total Cost of Application

Based upon the information contained in Section VIII of this report, the category as a whole would have to invest an estimated maximum of $10,000 to achieve limitations prescribed herein. There is also an anticipated increase in the operating cost equivalent to approximately 0.02 percent of the 1971 selling price of this product.

It is concluded that the benefits of the reduction of the discharge of pollutants by the selected control technology outweigh the costs. All of this industry category is presently achieving this level of pollutant discharge.

Age and Size of Equipment and Facilities

The best control technology currently available is practicable regardless of the size or age of plants since the use of existing technologies is not dependent on these factors. Also, the similarities in the process used and wastewater characteristics in this production category substantiate the practicality of these technologies.

Process Employed

The process used by the plants in this category are very similar in nature and their raw wastes are also quite similar. These similarities will enhance the application of the recommended treatment technologies.

Engineering Aspects

From an engineering standpoint, the implementation of the recommended best control technologies currently available is practicable in this production category because it is presently used in plants discharging process waste water.

Process Changes

The recommended control technologies would require no major changes in the manufacturing process. These control technologies are presently being used by plants in this production category.

Non-Water Quality Environmental Impact

The single major impact on non-water quality factors of the environment is the potential effect of land disposal of the solids removed from the process wastewaters. These solids may sometimes contain harmful constituents which could be detrimental to the soil system in the area of disposal or possibly contaminate ground waters due to rainwater run-off and percolation through the soil. There appear to be no major energy requirements for the implementation of the recommended treatment technologies.

Category II - Other Calcium Carbide Furnaces

Based upon the information contained in Sections III through VIII, a determination has been made that the degree of effluent reduction attainable through the application of the best practicable control technology currently available is no discharge of pollutants in process wastewater. Pollutants for this category are defined as: total suspended solids and pH above 9.0.

Identification of BPCTCA

Best practicable control technology currently available is to settle scrubber wastes in ponds and recycle to scrubber for those plants using wet scrubbing. Those plants using dry or no dust collection have no process waste water discharge.

Reason for Selection

One hundred percent (100%) of the industry category is presently achieving this level.

Total Cost of Application

Based upon the information contained in Section VIII of this report, the category as a whole would not have any additional investment to achieve the limitations prescribed herein. There is also no anticipated increase in the operating cost.

It is concluded that the benefits of the total elimination of the discharge pollutants by the selected control technology outweigh the costs. All of this industry category is presently achieving this level of pollutant discharge.

The best control technology currently available is practicable regardless of the size or age of plants since the use of existing technologies is not dependent on these factors.

Engineering Aspects

From an engineering standpoint, the implementation of the recommended best control technologies currently available is practicable in this category because it is currently in use.

Process Changes

The recommended control technologies would not require changes in the manufacturing process. These control technologies are presently being used by plants in this category.

Non-Water Quality Environmental Impact

The single major impact of non-water quality factors on the environment is the potential effect of land disposal of the solids removed from the process wastewaters. These solids may sometimes contain harmful constituents which could be detrimental to the soil system in the area of disposal or possibly contaminate ground waters due to rainwater run-off and percolation through the soil. There appear to be no major energy requirements for the implementation of the recommended treatment technologies.

SECTION X

EFFLUENT REDUCTION ATTAINABLE THROUGH THE APPLICATION OF THE BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE

The effluent limitations which must be achieved by July 1, 1983 are based on the degree of effluent reduction attainable through the application of the best available technology economically achievable. For the calcium carbide industry, this level of technology was based on the best control and treatment technology readily transferable from one industry process to another.

The following factors were taken into consideration in determining the best available technology economically achievable:

a) the age of equipment and facilities involved;

b) the process employed;

c) the engineering aspects of the application of various types of control techniques;

d) process changes;

e) cost of achieving the effluent reduction resulting from application of BATEA; and

f) non-water quality environmental impact (including energy requirements).

In contrast to the best practicable control technology currently available, best available technology economically achievable assesses the availability in all cases of in-process controls as well as control or additional treatment techniques employed at the end of a production process. In-process control options available which were considered in establishing these control and treatment technologies include the following:

a) alternative water uses

b) water conservation

c) waste stream segregation

d) water reuse

e) cascading water uses

f) by-product recovery

g) reuse of wastewater constituents

h) waste treatment

i) good housekeeping

j) preventive maintenance

k) quality control (raw material, product, effluent)

l) monitoring and alarm systems.

Although economic factors are considered in this development, the costs for this level of control are intended to be for the top-of-the-line of current technology subject to limitations imposed by economic and engineering feasibility. However, this technology may necessitate some industrially sponsored development work prior to its application.

Based upon the information contained in Sections III through IX of this report, the following determinations were made on the degree of effluent reduction attainable with the application of the best available control technology economically achievable in the various categories of this industry.

GENERAL WATER GUIDELINES

Process water is defined as any water contacting the reactants, intermediate products, by-products or products of a process including contact cooling water. All values of guidelines and limitations presented below are for total suspended solids (TSS) and harmful pollutants are expressed as a maximum 30 day average in units of kilograms of pollutant per metric ton (pounds of pollutant per thousand pounds) of product. The daily maximum limitation is double the 30 day average, except for pH. All process water effluents are limited to the pH range of 6.0 to 9.0 unless otherwise specified.

Based on the application of best available technology economically achievable, the recommendations for the discharge of such cooling water are as follows.

An allowed discharge of all non-contact cooling waters provided that the following conditions are met:

a) Thermal pollution be in accordance with standards to be set by EPA policies.

b) All non-contact cooling waters should be monitored to detect leaks from the process. Provisions should be made for treatment to the standards established for the process wastewater discharges prior to release.

c) No untreated process waters be added to the cooling waters prior to discharge.

The above non-contact cooling water recommendations should be considered as interim, since this type of water plus blowdowns from water treatment, boilers and cooling towers will be regulated by EPA at a later date as a separate category.

PROCESS WASTE WATER GUIDELINES AND LIMITATIONS

The other calcium carbide furnaces category was required to achieve no discharge of process wastewater pollutants to navigable waters based on best practicable control technology currently available. The same limitations are required based on best available technology economically achievable.

Category I - Covered Calcium Carbide Furnaces With Wet Air Pollution Control Devices

Based upon the information contained in Sections III through VIII, a determination has been made that the degree of effluent reduction attainable through the application of the best available control technology economically achievable is:

Effluent Characteristic	Effluent Limitation kg/kkg (lb/1000 lb)
TSS	0.11
Cyanide (Total)	0.0028
pH	6.0 to 9.0

The above limitations were based on an average process wastewater discharge of 7,500 liters per metric ton (1,800 gallons per ton).

Identification of BATEA

Best available control technology economically achievable for the manufacture of calcium carbide by the covered furnace process is the treatment of wet scrubbing effluent by chlorination, clarification, neutralization, and polish filtration where scrubbing is used.

To implement this technology at plants not already using the recommended control techniques would require the addition of chlorination equipment, clarifier-thickeners, neutralization facilities, sand filters, and the necessary piping and pumps.

Reason for Selection

Most of the recommended technology is presently being used in the plants within the category. The polish filtration technology is presently being used in the inorganic chemical and ferroalloys industries for treating waste water and the technology is transferable.

Total Cost of Application

Based upon the information contained in Section VIII of this report, the category as a whole would have to invest up to an estimated maximum of $168,000 to achieve limitations prescribed herein. There is also an anticipated increase in the operating cost equivalent to approximately 0.2 percent of the selling price of this product.

It is concluded that the benefits of the elimination/reduction of the discharge pollutants by the selected control technology outweigh the costs.

Age and Size of Equipment and Facilities

The best available technology economically achievable is practicable regardless of the size or age of plants since the use of existing technologies is not dependent on these factors. Also, the similarities in processes used and wastewater characteristics in this production category substantiate the practicality of these technologies.

Process Employed

The processes used by the plants in this category are very similar in nature and their raw wastes are also quite similar. These similarities will enhance the application of the recommended treatment technologies.

Engineering Aspects

From an engineering standpoint, the implementation of the recommended best available technology economically achievable is practicable in this category because all of the technology is in use in one plant of the category with the exception of polish filtration. This technology is readily available and transferable to treatment of calcium carbide scrubber wastes.

Process Changes

The recommended control technologies would not require major changes in the manufacturing process. These control technologies are presently being used by plants in both the ferroalloys and chemicals industries.

Non-Water Quality Environmental Impact

The single major impact on non-water quality factors of the environment is the potential effect of land disposal of the solids removed from the process wastewaters. These solids may sometimes contain harmful constituents which could be detrimental to the soil system in the area of disposal or possibly contaminate ground waters due to rainwater run-off and percolation through the soil. There appear to be no major energy requirements for the implementation of the recommended treatment technologies.

SECTION XI

NEW SOURCE PERFORMANCE STANDARDS AND PRETREATMENT STANDARDS

This level of technology is to be achieved by new sources. The term "new source" is defined in the Act to mean "any source, the construction of which is commenced after the publication of proposed regulations prescribing a standard of performance". This technology is evaluated by adding to the consideration underlying the identification of best available technology economically achievable, a determination of what higher levels of pollution control are available through the use of improved production processes and/or treatment techniques. Alternative processes, operating methods or other alternatives were considered. The end result of the analysis identifies effluent standards which reflect levels of control achievable through the use of improved production processes (as well as control technology).

The following factors were considered with respect to production processes which were analyzed in assessing the best demonstrated control technology currently available for new sources:

a) the type of process employed and process changes;

b) operating methods;

c) use of alternative raw materials and mixes of raw materials;

d) use of dry rather than wet processes; and

e) recovery of pollutants as by-products.

In addition to the effluent limitations covering discharges directly into waterways, the constituents of the effluent discharge from a plant within the industrial category which would interfere with, pass through, or otherwise be incompatible with a well designed and operated publicly owned activated sludge or trickling filter wastewater treatment plant were identified.

EFFLUENT REDUCTION ATTAINABLE BY THE APPLICATION OF THE BEST AVAILABLE DEMONSTRATED CONTROL TECHNOLOGIES, PROCESSES, OPERATING METHODS OR OTHER ALTERNATIVES

Based upon the information contained in Sections III through X of this report, the following determinations were made on the degree of effluent reduction attainable with the application of new source standards.

The other calcium carbide furnaces category was required to achieve no discharge of process wastewater pollutants to navigable waters based on best practicable control technology currently available. The same limitations are required for new source performance standards.

Category I - Covered Calcium Carbide Furnaces With Wet Air Pollution Control Devices

The only process water pollution involved in the manufacture of calcium carbide is that contributed by wet air pollution devices. For those covered furnaces operating with withdrawal and cleaning of unburned gas, the use of a baghouse collector is not considered practicable technology. However, these furnaces can operate with scrubbers and recycle the scrubber effluent. This technology is currently being practiced by one plant in the industry and another plant plans to install this treatment technology. Therefore the recommendations for new source performance standards are as follows:

Effluent Characteristic	Effluent Limitation kg/kkg (lb/1000 lb)
TSS	0.020
Cyanide (Total)	0.0005
pH	6.0 to 9.0

The above limitations were based on an average process wastewater blowdown for discharge of 1350 liters per metric ton (325 gallons per ton).

Identification of BADCTCA

Best available demonstrated control technology currently available for the manufacture of calcium carbide in covered furnaces with scrubbers is the treatment of wet scrubbing effluent by chlorination, clarification, neutralization, polish filtration and partial recirculation.

Reason for Selection

Most of the recommended technology is presently being used in plants within the ferroalloys industry. The polish filtration technology is presently being used in the inorganic chemical industry for treating waste water and the technology is transferable.

Age and Size of Equipment and Facilities

The best available demonstrated control technology currently available is practicable regardless of the size or age of plants since the use of existing technologies is not dependent on these factors. Also, the similarities in processes used and wastewater characteristics in this production category substantiate the practicality of these technologies.

Process Employed

The processes used by the plants in this category are very similar in nature and their raw wastes are also quite similar. These similarities will enhance the application of the recommended treatment technologies.

Engineering Aspects

From an engineering standpoint, the implementation of the recommended best available demonstrated control technology currently available is practicable in this category because all of the technology is in use in the industry with the exception of polish filtration. This technology is readily available and transferable to treatment of calcium carbide scrubber wastes.

Process Changes

The recommended control technologies would not require major changes in the manufacturing process. These control technologies are presently being used by plants in both the ferroalloys and chemicals industries.

Non-Water Quality Environmental Impact

The single major impact on non-water quality factors of the environment is the potential effect of land disposal of the solids removed from the process wastewaters. These solids may sometimes contain harmful constituents which could be detrimental to the soil system in the area of disposal or possibly contaminate ground waters due to rainwater run-off and percolation through the soil. There appear to be no major energy requirements for the implementation of the recommended treatment technologies.

PRETREATMENT STANDARDS FOR NEW SOURCES

Recommended pretreatment guidelines for discharge of plant wastewater into public treatment works conform in general with EPA Pretreatment Standards for Municipal Sewer Works as published in the July 19, 1973 Federal Register and "Title 40 - Protection of the Environment, Chapter I - Environmental Protection Agency, Subchapter D - Water Programs, Part 128 - Pretreatment Standards", a subsequent EPA publication. The following definitions conform to these publications:

a) Compatible Pollutant

The term "compatible pollutant" means biochemical oxygen demand, suspended solids, pH and fecal coliform bacteria, plus additional pollutants identified in the NPDES permit if the publicly owned treatment works was designed to treat such pollutants, and, in fact, does remove such pollutants to a substantial degree. Examples of such additional pollutants may include:

chemical oxygen demand
total organic carbon
phosphate and phosphorus compounds
nitrogen and nitrogen compounds
fats, oils, and greases of animal or vegetable origin except as defined below under Prohibited Wastes.

b) Incompatible Pollutant

The term "incompatible pollutant" means any pollutant which is not a compatible pollutant as defined above.

c) Joint Treatment Works

Publicly owned treatment works for both non-industrial and industrial wastewater.

d) Major Contributing Industry

A major contributing industry is an industrial user of the publicly owned treatment works that: has a flow of 50,000 gallons or more per average work day; has a flow greater than five percent of the flow carried by the municipal system receiving the waste; has in its waste, a toxic pollutant in toxic amounts as defined in standards issued under Section 307(a) of the Act; or is found by the permit issuance authority, in connection with the issuance of an NPDES permit to the publicly owned treatment works receiving the waste, to have significant impact, either singly or in combination with other contributing industries, on that treatment works or upon the quality of effluent from that treatment works.

e) Pretreatment

Treatment of wastewaters from sources before introduction into the joint treatment works.

PROHIBITED WASTES

No waste introduced into a publicly owned treatment works shall interfere with the operation or performance of the works. Specifically, the following wastes shall not be introduced into the publicly owned treatment works:

a) Wastes which create a fire or explosion hazard in the publicly owned treatment works;

b) Wastes which will cause corrosive structural damage to treatment works, but in no case wastes with a pH lower than 5.0, unless the works are designed to accommodate such wastes;

c) Solid or viscous wastes in amounts which would cause obstruction to the flow in sewers, or other interference with the proper operation of the publicly owned treatment works, and

d) Wastes at a flow rate and/or pollutant discharge rate which is excessive over relatively short time periods so that there is a treatment process upset and subsequent loss of treatment efficiency.

PRETREATMENT FOR INCOMPATIBLE POLLUTANTS

In addition to the above, the pretreatment standard for incompatible pollutants introduced into a publicly owned treatment works by a major contributing industry shall be best practicable control technology currently available; provided that, if the publicly owned treatment works which receives the pollutants is committed, in its NPDES permit, to remove a specified percentage of any incompatible pollutant, the pretreatment standard applicable to users of such treatment works shall be correspondingly reduced for that pollutant; and provided further that the definition of best practicable control technology currently available for industry categories may be segmented for application to pretreatment if the Administrator determines that the definition for direct discharge to navigable waters is not appropriate for industrial users of joint treatment works.

RECOMMENDED PRETREATMENT GUIDELINES

In accordance with the preceding Pretreatment Standards for Municipal Sewer Works, the following are recommended for Pretreatment Guidelines for the wastewater effluents:

a) No pretreatment required for removal of compatible pollutants - biochemical oxygen demand, suspended solids (unless hazardous), pH and fecal coliform bacteria;

b) Suspended solids containing hazardous pollutants (such as heavy metals, cyanides and chromates) should be restricted;

c) Pollutants such as chemical oxygen demand, total organic carbon, phosphorus and phosphorus compounds, nitrogen and nitrogen compounds and fats, oils and greases need not be removed provided the publicly owned treatment works was designed to treat such pollutants and will accept them. Otherwise levels should be at or below BPCTCA Guideline levels;

d) Dissolved solids such as sodium chloride, sodium sulfate, calcium chloride and calcium sulfate should be permitted provided that the industrial plant is not a "major contributing industry".

e) Plants covered under the "major contributing industry" definition should not be permitted to discharge large quantities of dissolved solids into a public sewer. Each of these cases would have to be considered individually by the sewer authorities, and,

f) Discharge of all other incompatible hazardous or toxic pollutants from the chemical plants of this study to municipal sewers should conform to BPCTCA guidelines for discharge to surface water.

SECTION XII

ACKNOWLEDGEMENTS

This report was prepared by the Environmental Protection Agency on the basis of a comprehensive study performed by General Technologies Corporation under contract # 68-01-1513. Dr. Robert Shaver, Project Manager, assisted by Mr. Lee McCandless, prepared the original (Contractor's) report.

This study was conducted under the supervision and guidance of Elwood E. Martin, Project Officer for inorganic chemicals, assisted by Patricia W. Diercks, Project Officer for ferroalloys.

Overall guidance and assistance was provided by the author's associates in the Effluent Guidelines Division, particularly Messrs. Allen Cywin, Director, Ernst P. Hall, Deputy Director, and Walter J. Hunt, Branch Chief.

The cooperation of the carbide producers who offered their plants for survey and contributed pertinent data is gratefully appreciated. The operations and the plants visited were the property of the following companies:

Airco Alloys and Carbide
Midwest Carbide Corporation
Pacific Carbide Corporation
Union Carbide Corporation

Acknowledgement and appreciation is also given to Ms. Patsy Williams of the EGD secretarial staff and to the secretarial staff of General Technologies Corporation for their efforts in the typing of drafts, necessary revisions, and the final preparation of this and the contractor's draft document.

Thanks are also given to the members of the EPA Working Group/Steering Committee for their advice and assistance. They are: Messrs. D. Fink, Ms. N. Speck, Dr. H. Durham and Walter J. Hunt.

SECTION XIII

REFERENCES

1. Compilation of Air Pollutant Emission Factors, U.S. Environmental Protection Agency, Office of Air Programs, February, 1973 (N.T.I.S. No. PB-209 559).

2. Test Number 72-PC-07 at Union Carbide Corporation Ferroalloys Division, Ashtabula, Ohio, June 1972, Resources Research, Inc. McLean, Va. 22101 (Contract CPA 70-81).

3. Sherman, P. R. & Springman, E. R., "Operating Problems with High Energy Wet Scrubbers on Submerged Arc Furnaces", a paper presented at the American Institute of Metallurgical Engineers Electric Furnace Conference, Chicago, Illinois December, 1972.

4. "Encyclopedia of Chemical Technology", 3rd ed., R. Kirk and D.F. Othmer, eds. McGraw-Hill Book Company, New York, N.Y. (1965).

5. "Current Industrial Reports - Inorganic Chemicals, 1971", Bureau of the Census, U.S. Department of Commerce, Series: M28A(71)-14 (October, 1972).

6. "Detection and Measurement of Stream Pollution," Contained in Biology of Water Pollution. Federal Water Pollution Control Administration, 1967.

7. Lund, Herbert F., Industrial Pollution Control Handbook, McGraw Hill Book Co., New York, N.Y.

8. Trace Metals in Waters of the United States, Federal Water Pollution Control Administration, 1967.

9. Handbook for Monitoring Industrial Wastewater, U.S. Environmental Protection Agency, August 1973.

10. Unpublished Communications, Calgon Corporation, Pittsburgh, Pa. - Cyanide Treatment.

11. "Development Document for Proposed Effluent Limitations Guidelines and New Source Performance Standards - Smelting and Slag Processing Segments of the Ferroalloy Point Source Category", Effluent Guidelines Division Report EPA-440/1-73-008 (August, 1973), Office of Air and Water Programs, U.S. Environmental Protection Agency, Washington, D.C. 20460.

12. "Development Document for Proposed Effluent Limitations Guidelines and New Source Performance Standards - Significant Inorganic Products Segment of the Inorganic Chemicals Manufacturing Point Source Category". Effluent Guidelines Division Contract No. 68-01-1513 (December, 1973), Office of Air and Water Programs, U.S. Environmental Protection Agency, Washington, D.C. 20640.

13. Oil, Paint, and Drug Reporter, December 15, 1969 and February 22, 1971.

SECTION XIV

GLOSSARY

Covered furnace - An electric furnace with a water-cooled cover over the top to limit the introduction of air which would burn the gases from the reduction process. The furnace may have sleeves at the electrodes (fixed seals or sealed furnaces) with the charge introduced through ports in the furnace cover, or the charge may be introduced through annular spaces surrounding the electrodes (mix seals or semi-closed furnace).

Ferroalloy - An intermediate material, used as an addition agent or charge material in the production of steel and other metals. Historically, these materials were ferrous alloys, hence the name. In modern usage, however, the term has been broadened to cover such materials as silicon metal, which are produced in a manner similar to that used in the production of ferroalloys.

Open furnace - An electric submerged-arc furnace with the surface of the charge exposed to the atmosphere, whereby the reaction gases are burned by the inrushing air.

Reducing Agent - Carbon bearing materials, such as metallurgical coke, low volatile coal, and petroleum coke used in the electric furnace to provide the carbon which combines with oxygen in the charge to form carbon monoxide, thereby reducing the oxide to the metallic form.

Self-baking electrode - The electrode consists of a sheet steel casing filled with a paste of carbonaceous material quite similar to that used to make prebaked amorphous carbon electrodes. The heat from the passage of current within the electrode and the heat from the furnace itself, volatilize the asphaltic or tar binders in the paste to make a hard-baked electrode.

Sintering - The formation of larger particles, cakes, or masses from small particles by heating alone, or by heating and pressing, so that certain constituents of the particles coalesce, fuse, or otherwise bind together. This may occur in the furnace itself, in which case the charge must be stoked to break up the agglomeration.

Submerged-arc furnace - In ferroalloy reduction furnaces, the electrodes usually extend to a considerable depth into the charge, hence such furnaces are called "submerged-arc furnaces". This name is used for the furnaces whose load is practically entirely of the resistant type.

Tapping - This term is used in the metallurgical industries for the removal of molten metal from furnaces, usually by opening a taphole located in the lower portion of the furnace vessel.

TABLE 3

CONVERSION FACTORS

Multiply (English Units)		by		To Obtain (Metric Units)
English Unit	Abbreviation	Conversion	Abbreviation	Metric Unit
acres	ac	0.405	ha	hectares
acre-feet	ac ft	1233.5	cu m	cubic meters
British Thermal Unit	BTU	0.252	kg cal	kilogram-calories
British Thermal Unit/pound	BTU/lb	0.555	kg cal/kkg	kilogram-calories/kilogram
cubic feet/minute	cfm	0.028	cu m/min	cubic meters/minute
cubic feet/second	cfs	1.7	cu m/min	cubic meters/minute
cubic feet	cu ft	0.028	cu m	cubic meters
cubic feet	cu ft	28.32	l	liters
cubic inches	cu in	16.39	cu cm	cubic centimeters
degree Fahrenheit	°F	0.555(°F-32) [a]	°C	degree Centigrade
feet	ft	0.3048	m	meters
gallon	gal	3.785	l	liters
gallon/minute	gpm	0.0631	l/sec	liters/second
horsepower	hp	0.7457	kw	kilowatts
inches	in	2.54	cm	centimeters
inches of mercury	in Hg	0.03342	atm	atmospheres
pounds	lb	0.454	kg	kilograms
million gallons/day	mgd	3,785	cu m/day	cubic meters/day
mile	mi	1.609	km	kilometer
pound/square inch (gauge)	psig	(0.06805 psig +1) [a]	atm	atmospheres (absolute)
square feet	sq ft	0.0929	sq m	square meters
square inches	sq in	6.452	sq cm	square centimeters
tons (short)	t	0.907	kkg	metric tons (1000 kilograms)
yard	y	0.9144	m	meters

(a) Actual conversion, not a multiplier