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

SMELTING AND SLAG PROCESSING

Segments of the Ferroalloy Manufacturing Point Source Category

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U.S. ENVIRONMENTAL PROTECTION AGENCY Washington, D.C. 20460 DEVELOPMENT DOCUMENT

for

EFFLUENT LIMITATIONS GUIDELINES

and

NEW SOURCE PERFORMANCE STANDARDS

FOR THE SMELTING AND SLAG PROCESSING

SEGMENTS OF THE

FERROALLOY MANUFACTURING POINT SOURCE CATEGORY

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ABSTRACT

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

- I Open Electric Furnaces with Wet Air Pollution Control Devices
- II Covered Electric Furnaces and Other Smelting Operations with Wet Air Pollution Control Devices
- III Slag Processing

The effluent limitations to be achieved by July 1, 1977 are based upon the pollution reduction attainable using those treatment technologies as presently practiced by the average of the best plants in these categories, unless present technology is uniformly inadequate within a category. The technologies are for the most part based upon the use of 'end of pipe' treatment and once-through water usage.

The effluent limitations to be achieved by July 1, 1983 are based upon the pollution reduction attainable using those control and treatment technologies as presently practiced by the best plant in the category, or readily transferrable from one industry process to another.

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.

Costs are given for the various levels of treatment identified for each category and for the attainment of the suggested effluent guidelines and new source performance standards.

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SECTION I

CONCLUSIONS

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

- I Open Electric Furnaces with Wet Air Pollution Control Devices
- II Covered Electric Furnaces and Other Smelting Operations with Wet Air Pollution Control Devices
- III Slag Processing

Other factors, such as age, size of plant, geographic location, product, and waste control technologies do not justify segmentation of the industry into any further subcategories for the purpose of establishing effluent limitations and standards of performance. Similarities in waste loads and available treatment and control technologies within the categories further substantiate this. The guidelines for application of the effluent limitations and standards of performance to specific plants take into account the mix of furnace types and water uses possible in a single plant which directly influence the quantitative pollutional load.

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SECTION II

RECOMMENDATIONS

It is recommended that the effluent limitations guidelines and new source performance standards be adopted as suggested herein for the ferroalloy 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.

The application of these guidelines and performance standards to specific plants is intended to be on the basis of a "building block" approach to define the effluent limits from the plant as a whole. Consider, for example, a large ferroalloy plant having one or more of the processes and/or water uses in each category. The total effluent limitation for the plant would be based upon the total of the allowable loads for each category, determined by multiplying the allowable unit load by the total production rate in that category. It is recommended that this method of application of the guidelines and performance standards be used.

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 or use in electrolytic processes, 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:

- I Physical/chemical treatment to remove or destroy suspended solids and potentially harmful or toxic pollutants, with recirculation of water at the scrubber.
- II Physical/chemical treatment to remove or destroy suspended solids and potentially harmful or toxic pollutants.
- III Physical/chemical treatment to remove suspended solids and potentially harmful pollutants.

The effluent limitations are based on achieving by July 1, 1977 at least the pollution reduction attainable using these treatment technologies as presently practiced by the average of the best plants in these categories. The above technologies are generally based upon the use of 'end of pipe' treatment and once-through water usage. The 30 day average effluent limitations corresponding to the best practicable control technology currently available are as follows, by category:

	Categ I	ory	_	egory I	Ca	ategory III
	kg/ mwhr	1b/ mwhr	kg∕ mwhr	1b∕ mwhr	kg/ kkg pr	lb/ . ton pr.
Suspended Solid Total Chromium	.0032	.352 .007	.209 .004	.461	1.330 .026	2.659 .053
Hex. Chromium	.0003	.0007	.0004	.0009	-	-
Cyanide Manganese	.032	.070	.002 .042	.005 .092	.266	.532
Phenol		-	.004	.009	-	-
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The best available technology economically achievable for existing point source is as follows, by category:

- I Partial recycle of water, with blowdown treated for removal of suspended solids and potentially harmful or toxic pollutants by physical/chemical treatment.
- II Partial recycle of water, with blowdown treated for removal of suspended solids and potentially harmful or toxic pollutants by physical/chemical treatment.
- III Partial recycle of water, with blowdown treated for removal of suspended solids and potentially harmful or toxic pollutants by physical/chemical treatment.

The effluent limitations are based on achieving by July 1, 1983, at least the pollution reduction using these control and treatment technologies as presently practiced by the best plant in each category, and using transfer of technology where the best plant in the category is felt to be insufficient.

The 30 day average effluent limitations corresponding to the best available technology economically achievable for Categories I, II and III are as follows:

	Categ	ory I	Categ	ory II	Cateq	ory III
	kg/mwhr	1b/mwhr	kg/mwhr	lb/mwhr	kg/kkg p	or. 1b/ton pr.
Suspended Solids	.012	.026	.016	.035	.136	.271
Total Chromium	.0004	.0009	.0005	.0012	.0027	.0054
Hex. Chromium	.00004	.0001	.00005	.0001	-	-
Total Cyanide	-	-	.0003	.0006	-	-
Manganese	.0039	.0086	.005	.012	•02 7	.054
Phenol	-	-	.0002	.0005	-	-
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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. The best available demonstrated control technology for new sources is the same as the best available technology economically achievable, which will be utilized to meet the 1983 limitations.

The 30 day average standard of performance for new sources, which corresponds to the application of best available demonstrated control technology, process, operating methods or other alternatives for Categories I, II and III are as follows:

	Catego	ory I	Catego	ry II	Catego	ry III
	kg/mwhr	1b/mwhr	kg/mwhr	lb/mwhr	kg/kkg pr	. 1b/ton pr.
Suspended Solids	.012	.026	.016	.035	.136	. 271
Total Chromium	.0004	.0009	.0005	.0012	.0027	.0054
Hex. Chromium	.00004	.0001	.00005	.0001	-	-
Total Cyanide	-	-	.0003	.0006	-	-
Manganese	.0039	.0086	.005	.012	.027	.054
Phenol	-	-	.0002	.0005	-	-
рн	6	- 9	6	- 9	6 -	9

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SECTION III

INTRODUCTION

The Federal Water Pollution Control Act Amendments of 1972 (the "Act") requires the United States Environmental Protection Agency to establish effluent limitations which must be achieved by point sources of discharge into the navigable waters of the United States. Section 301 of the Act requires the achievement by July 1, 1977, of effluent limitations which require the application of the "best practicable control technology currently available," and the achievement by July 1, 1983, of effluent limitations which require the application of the "best available technology economically achievable."

Within one year of enactment, the Administrator is required by Section 304(b) to promulgate regulations providing guidelines for the effluent limitations required to be achieved under Section 301 of the Act. These regulations are to identify in terms of amounts of constituents and chemical, physical, and biological characteristics of pollutants, the degree of effluent reduction attainable through the application of the best practicable control technology currently available and best available technology economically achievable. The regulations must also specify factors to be taken into account in identifying the two statutory technology levels and in determining the control measures and practices which are to be applicable to point sources within given industrial categories or classes to which the effluent limitations apply.

In addition to his responsibilities under Sections 301 and 304 of the Act, the Administrator is required by Section 306 to promulgate standards of performance for new sources. These standards are to reflect 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."

The Office of Air and Water Programs of the Environmental Protection Agency has been given the responsibility by the Administrator for the development of effluent limitation guidelines and new source standards as required by the Act. The Act requires the guidelines and standards to be developed within very strict deadlines and for a broad range of industries. Effluent limitations guidelines under Section 301 and 304 of the Act and standards of performance for new sources under Section 306 of the Act will be developed for 27 industrial categories. Moreover, each of these industrial categories probably will require further subcategorization in order to provide standards that are meaningful. In order to promulgate the required guidelines and standards, it is necessary to (a) categorize each industry; (b) characterize the first resulting from discharges within industrial categories waste and subcategories; and (c) identify the range of control and treatment technology within each industrial category and subcategory. Such technology will then be evaluated in order to determine what constitutes "best practicable control technology currently available," what is the the "best available technology economically achievable" and, for new sources, what is the "best available demonstrated control technology."

In identifying the technologies to be applied under Section 301, Section 304 (b) of the Act requires that the cost of application of such technologies be considered, as well as the non-water quality environmental impact (including energy requirements) resulting from the application of such technologies. It is imperative that the effluent limitations and standards to be promulgated by the Administrator be verifiable data and that there be a supported by adequate, sound judgments made. rationale for the Such data must be readily identifiable and available and such rationale must be clearly set forth in the documentation supporting the regulations.

FERROALLOY MANUFACTURE

Ferroalloys are used for deoxidation, alloying, and graphitization of steel and cast iron. In the nonferrous metal industry, silicon is used primarily as an alloying agent for copper, aluminum, magnesium, and nickel. Seventy five percent ferrosilicon is used as a reducing agent in the production of magnesium by the Pidgeon process. Manganese is the most widely used element in ferroalloys, followed by silicon and chromium. Others include molybdenum, tungsten, titanium, zirconium, vanadium, boron, and columbium.

There are four major methods used to produce ferroalloy and high purity metallic additives for steelmaking. These are (1) blast furnace, (2) electric smelting furnace, (3) alumino- or silicothermic process and (4) The choice of process is dependent upon the electrolytic deposition. alloy produced and the availability of furnaces. Ferromanganese is the principal metallurgical form of manganese. This product contains 75% or more of manganese, the balance being mainly iron. It is produced in the furnace or electric-arc furnace and is available in several blast grades. A few steel companies produce ferromanganese for their own use since they have their own ore sources and suitable blast furnaces available. The production of ferromanganese in blast furnaces is a part of S.I.C. 3312 and such production is not considered herein, but will be covered under the guidelines for the iron and carbon steel industry. Electric smelting furnaces produce most of the ferroalloy tonnage.

The majority of electric ferroalloy furnaces are termed submerged arc, although the mode of energy release in many cases is resistive heating. Raw ore, coke, and limestone or dolomite mixed in proper proportions constitute the charge for the electric-arc furnace process. A large supply of electric power is necessary for economical operation. Important operating considerations include power and electrode requirements, size and type of furnace, amount and size of coke, and slag losses. The major ferroalloys thus produced are:

- Silicon Alloys Ferrosilicon (50-98% Si) and Calcium Silicide
- 2. Chromium Alloys High carbon Ferrochromium in various grades and Ferrochromesilicon.
- 3. Manganese Alloys Standard Ferromanganese and Silicomanganese

There are a smaller number of furnaces which do not operate with deep submergence of the electrodes and produce a batch melt which is usually removed by tilting the furnace. Mix additions and power input would usually be cyclic. Examples of products produced in this type of furnace are:

- 1. Manganese Ore-Lime melt for subsequent ladle reactions with silicomanganese to produce medium carbon and low carbon ferromanganese.
- 2. Chrome Ore-Lime melt for subsequent ladle reaction with ferrochromesilicon to produce low carbon ferrochromium.
- 3. Special Alloys, such as Aluminum Vanadium, Ferrocolumbium, Ferroboron, Ferrovanadium and Ferromolybdenum.

The largest source of waterborne pollutants other than thermal in the industry is the use of wet methods for air pollution control; consideration of air pollution sources is thus of importance here. The production of ferroalloys has many dust or fume producing steps. Particulates are emitted from raw materials handling, mix delivery, crushing, grinding, and sizing, and furnace operations. Emissions from furnaces vary widely in type and quality, depending upon the particular ferroalloy being produced and the type of furnace used.

The conventional submerged-arc furnace utilizes carbon reduction of metallic oxides and continuously produces large quantities of carbon monoxide. Other sources of gas are moisture in the charge materials, reducing agent volatile matter, thermal decomposition products of the raw ore, and intermediate products of reaction. The carbon monoxide content of the furnace off-gas varies from 50-90% by volume, depending upon the alloy being produced and the amount of furnace feed pretreatment. The gases rising out the top of the furnace carry fume or fume precursors and also entrain the finer size constituents of the mix or charge. Submerged-arc furnaces operate in steady-state and gas generation is continuous. In an open furnace, all the CO burns with induced air at the top of the charge, resulting in a large volume of gas. In a covered or closed furnace most or all of the CO is withdrawn from the furnace without combustion with air. The controls used are thus affected by the type of furnace, the gas volume and emitted particle size and particle characteristics.

Fume emission also occurs at furnace tap holes. Because most furnaces are tapped intermittently, tap hole fumes occur only about 10 to 20% of the furnace operating time. Melting operations may be conducted in an open arc furnace (as opposed to a submerged arc furnace) in some plants. While no major quantities of gas are generated in this operation, thermally induced air flow may result in fume emission.

WATER POLLUTION SOURCES

Air pollution control devices include baghouses, wet scrubbers, and electrostatic precipitators. Wet scrubbers, of course, produce slurries containing most of the particulates in the off-gases. Spray towers used to cool and condition the gases before precipitators produce slurries containing some percentage of the particulates in the gases. Baghouses generally produce no wastewater effluents. In one plant, however, the gases from excthermic processes are cooled by water sprays, scrubbed in wet dynamic scrubbers, and finally cleaned in a baghouse in which the bags are periodically washed with water.

The only currently feasible type of wet collector for cleaning the large gas volume from open furnaces is the venturi type scrubber. With required pressure drops on the order of 152.4 cm (60 in.) W.G., the power consumption approaches 10% of the furnace rating. Most venturi designs allow recirculation of scrubbing liquor SO that water consumption is reduced to that evaporated into the gas plus that exiting with the concentrated solids stream. The venturi has the advantage of being able to absorb gas temperature peaks by evaporating more water. For a ferrosilicon or ferrochromesilicon operation substantially all of the sulfur in the reducing agent appears in the gas phase, and a corrosion problem occurs in any liquid recycle system unless neutralizing agents or special materials of construction are used.

Electrostatic precipitators have been installed on open furnaces producing ferrosilicon, ferrochromesilicon, high-carbon ferrochromium, and silicomanganese, both in this country and abroad. Most ferroalloy fumes at temperatures below 259.7°C (500°F) have too high an electrical resistivity, i.e., greater than 1 X 10¹⁰ ohm-cm for the use of electrostatic precipitators. The resistivity is in an accepted range only if the gas temperature is maintained above 259.7-315.2°C (500- $600^{\circ}F$). Water conditioning would lower the resistivity, but a large spray tower is required for proper humidification. Stainless steel construction would be a necessity for ferrosilicon or ferrochromesilicon operations. The alternate use of steam is feasible if low-cost steam is available.

The resistivity problem could be overcome by using a wet precipitator, but water usage appears to be greater than that for a wet scrubber without recycle. Wet electrostatic precipitators have been used at one installation in Europe. However, all parts of the precipitator exposed to the dirty water and to the wet gas were constructed of stainless steel. Electrostatic precipitators have found limited usage in American ferroalloy plants, although commonly used in Japan.

Submerged arc furnaces may be characterized as open, semi-closed, and sealed. The latter two types may also be termed covered furnaces. The open furnace has no cover and air is freely available to burn the CO coming off from the charge. The semi-closed furnace has a cover through which the electrodes extend down into the charge; the space around the electrodes is kept filled with the charge materials to form a quasi-seal which reduces the emissions from these locations but does not completely prevent the escape of the gases generated. The sealed furnace has a similar cover but with mechanical seals around both the electrodes, which do prevent the escape of gases.

The sealed furnace has thus far been applied only to calcium carbide, pig iron, standard ferromanganese and silicomanganese. In Japan, it has also been used to produce ferrochromium, ferrochromesilicon, and 50% and 75% ferrosilicon. Sealed covers are difficult to adapt to an existing furnace because of the extensive revisions that are usually required.

The disintegrator types of scrubber was formerly often employed for the cleaning of gases from covered furnaces. Although it can do a good cleaning jcb when properly maintained on furnaces producing calcium carbide, venturi scrubbers do a better job of dust removal for other products. The disintegrator type of scrubber has the advantage of producing a slight pressure head (about 5 cm (2 in.) W.G.), but the capacity limitations and high water and power consumption make it uneconomical for most new furnace installations. Additionally, the need for greater dust removal from furnace gases have caused disintegrator scrubbers to be eclipsed by venturi scrubbers.

The venturi type scrubber has been installed for cleaning CO gas from covered furnaces, but the required pressure drops are high (about 152 cm (60 in.)W.G.). The electrostatic precipitator is a possible CO gas cleaning device, but has found no such applications in the United States, although it is commonly used in Japan. It is possible to use a bag collector to clean CO gas, but only one such installation is known in the world, and none in this country. A "candle filter" system for cleaning CO gases in ceramic filters, is another (albeit rare) type of dry dust collectors. Other sources of wastewater in the industry are from cooling uses, boiler feed, air conditioning, and sanitary uses. Wastewaters also result from slag processing operations in which slag is crushed and sized for recovery of metal values, or from slag shotting operations in which the slag is granulated for further use.

PLANT LOCATIONS AND INDUSTRY STATISTICS

There are some 40 plants in the United States which produce ferroalloys, chromium, manganese, and other additive metals as tabulated in Table 1.

The <u>1967</u> <u>Census of Manufactures</u> reports 34 establishments in S.I.C. 3313, i.e., primarily engaged in the production of electrometallurgical products. Of these establishments, only 20 were included in the <u>1968</u> <u>Water Use in Manufacturing</u> data as having used 75.7 million liters (20 million gals.) or more of water annually. The total value of shipments in S.I.C. 3313 (34 plants) in 1967 was \$467.9 million. The value of shipments from the 20 large water-using plants was \$411.4 million.

Although according to the <u>Minerals Yearbook, 1970</u>, shipments rather than production are the measure of activity in the industry, as production in the high-volume ferroalloys may be irregular and intermittent, for air and water pollution regulatory purposes production is a better indicator of industry activity than is shipments. Production and shipments in 1970 were as shown in Table 2.

	Produ	iction		Shipments	
Product	<u>kkq</u>	tons	kkg	tons	Value (\$1000)
Ferrcmanganese Silicomanganese	757,920 175,285	835,463 193,219	732,283	807,368	134,456
Ferrosilicon	643,455	709,287	156,900 597,909	172,988 659,216	32,024 136,238
Silvery Iron Chromium Alloys:	178,143	196,369	188,351	207,664	16,853
Ferrochromium Other	280,876 87,238	309,613 96,163	262,481 73,968	289,395 81,552	100,667 25,606
Ferrctitanium	3,048	3,360	2,985	3,291	3,503
Ferrocolumbium Total	<u>1,143</u> 2,127,108	<u>1,260</u> 2,344,734	<u>1,289</u> 2,016,166	<u>1,421</u> 2,222,895	<u>9,385</u> 458,732

Table 2. FERROALLCY PRODUCTION AND SHIPMENTS IN 1970

		Plant				No.
	Producers	Size	Locations	Products	Type of furnace	Furnace
1	Air Reduction Co., Inc.	L	Calvert City, Ky.	FeCr, FeMn, FeSi, FeCrSi	Electric	11
2	Airco Alloys Div.	М	Charleston, S.C.	,	Electric	2
3		м	Niagara Falls, N.Y.		Electric	ī
Ļ		S	Theodore, Ala.		Electric	ī
	American Potash Co.	S	Aberdeen, Miss.	Min	Electrolytic	
	Chromium Mining & Smelting Co.	м	Woodstock, Tenn	FeMn,SiMn,FeSi,FeCr, FeCrSi	Electric	5
	Climax Molybdenum Co.	S	Langeloth, Pa.	FeMo	Aluminothermic	
	Foote Mineral Co.	S	Cambridge, Ohio	FeB,FeCb,FeTi,FeV,other	Electric	2
		L	Graham, W. Va.	FeCr, FeCrSi, FeSi, other	Electric	9
		М	Keokuk, Iowa	FeSi, Silvery Iron	Electric	5
		s	New Johnsonville, TN		Electrolytic	
		М	Steubenville, Ohio	FeCr, FeCrSi	Electric	6
		М	Wenatchee, Wash.	FeSi, Si	Electric	4
	Hanna Nickel Smelting Co.	S	Riddle, Oreg.	FeSi	Electric	4
		L	Beverly, Ohio	FeCr, FeSi, SiMn	Electric	7
	Kawecki Berylco Industries	S	Springfield, Oreg.	Si	Electric	2
	Kawecki Chemical Co.	S	Easton, Pa.	FeCb	Aluminothermic	
	Luckenby	S	Selma, Ala.	FeSi	Electric	1
	Manganese Chemicals Co., Diamond Shamrock	S	Kingwood, W. Va.	FeMn	Fused Salt Electro- lytic	
	Molybdenum Corp. of America		Washington, Pa.	FeMo	Electric & Alumino- thermic	
-	National Lead Co.	S	Niagara Falls,N.Y.	FeCbTi,FeTi,other	Electric	3
	New Jersey Zinc Co.	S	Palmerton, Pa.	Spiegeleisen	Electric	1
	Ohio Ferro Alloy Corp.	м	Brilliant, Ohio	FeCr,FeSi,Si,FeCrSi	Electric	4
 5		L	Philo, Ohio	FeB, FeMn, FeSi, SiMn, Si	Electric	10
		M S	Powhatan, Ohio	FeSi, Si	Electric	4
	Reynolds Metals Co.	S	Tacoma, Wash.	FeCr, FeSi Si	Electric Electric	2 1
	Reading Alloys	S	Lister Hill, Ala. Robesonia, Pa.	FeB, FeCb, FeV, NiCb, FeMo	Aluminothermic	1
	Sandgate Corp.	s	Houston, Texas	FeMn, SiMn	Electric	3
1	Shieldalloy Corp.	s	Newfield, N.J.	FeV, FeTi, FeB, FeMo, FeCb, FeCbTa	Aluminothermic	
	Tennessee Alloys Corp.	S	Bridgeport, Ala.	FeSi	Electric	3
:	Tennessee Metallurgical Co.	S	Kimball, Tenn.	FeSi	Electric	2
	Union Carbide Corp.	L,	Alloy, W. Va.	FeB,FeCr,FeCrSi,FeCb, FeSi, FeMn	Electric	16
ł		L	Ashtabula, Ohio	FeTi,FeW,FeV,SiMn,other	Electric	8
;		L	Marietta, Ohio		Electric, electrolytic,vacuum	11
5		s	Niagara Falls,N.Y.		Electric, aluminothermic	2
7		S	Portland, Oreg.		Electric	2
3		М	Sheffield, Ala.		Electric	5
9	Woodward Co.	м	Rockwood, Tenn.	FeMn, SiMn	Electric	7
)	Div. Mead Corp.	S	Woodward, Ala.	FeSi	Electric	1

Table 1. TYPES, SIZES, AND LOCATIONS OF FERROALLOY PRODUCING PLANTS IN THE UNITED STATES

a Plant size classification S-Up to 25,000 KW M- 25,000 to 75,000 KW L-Over 75,000 KW

•

In 1970, 345,567 kkgs (381,000 tons) of ferroalloys were produced in blast furnaces according to the <u>Annual Statistical Report</u>, <u>A.I.S.I.-</u><u>1570</u>. Plants using other than blast furnaces thus produced about 1,781,107 kkgs (1,963,734 tons) in that year.

On the basis of the census data and the number of plants enumerated in Table 1, the distribution of numbers of plants versus capacity in the industry appears to be as in Table 3.

Table 3. NUMBER OF PLANTS VS. VALUES OF SHIPMENTS-1967

	<u>Value_of_Shipmer</u>	nts (\$ million)
<u>No. of plants</u>	Ferroalloys	Total
20	-	411.4
34	398.2	467.9
40	420.4	-

The large water-using plants thus account for some 88 percent of the value of shipments in S.I.C. 3313, while numbering 20 out of 40 and apparently account for over 80 percent of the total value of the shipment of ferroalloys.

The <u>1968 Water Use in Manufacturing</u> data for those establishments using more than 75.7 million liters (20 million gal) of water annually are summarized in Tables 4 thru 9.

Table 4. WATER INTAKE, USE, AND DISCHARGE: 1968

No. of Establishments No. of Employees Value Added by Manufacture No. of Establishments Recirculating Wa	ater			20. 700. 168.9 2 17	x ´	106
	Lite	ers	3	<u> </u>	lor	<u>ns</u>
Total Intake Intake Treated Prior to Use Total Water Discharged Intake for Process Intake for Air Conditioning Intake for Steam Electric Power Intake for Other Cooling or Condensing Intake for Boiler Feed, Sanitary, etc.	757. 701.4 381.5	X X X X X X X X	106 109 109 109 109 109	900. 296.1 1.3 200. 185.3 100.8	X X X X X X X	106 109 109 109 109 109

Table 5. WATER INTAKE BY WATER USE REGION: 1968

	Inta	ake	
Region	109 liters	109 gals.	No. Establishments
Delaware and Hudson	(D)	(D)	(D)
Eastern Great Lakes	381.5	100.8	5
Ohio River	684.3	180.8	7
Tennessee	(D)	(D)	(D)
Southeast	(D)	(D)	(D)
Upper Mississippi	(D)	(D)	(D)
Pacific Northwest	(D)	(D)	(D)

(D) Withheld to avoid disclosing data on individual plants.

Table 6. WATER INTAKE, USE, AND DISCHARGE: 1968

Value of Shipments \$411.4 X 10° <u>Liters</u> <u>Gallons</u> Intake from Public Systems 3028. X 106 800. X 106 1119.2 X 109 295.7 X 109 Co. Surface Intake Co. Ground Intake 6.4 X 109 X 109 1.7 1212.3 X 109 1514. X 106 X 109 Gross Water Used 320.3 400. X 10° Public Sewer Discharge Surface Water Discharge 1102.2 X 109 291.2 X 109 500. Ground Water Discharge 1892.5 X 104 X 106 15.5 X 109 X 109 Transferred to other Users 4.1 Treated before Discharge 199.4 X 109 52.7 X 109

Table 7. INTAKE, USE, AND DISCHARGE BY WATER USE REGION: 1968

Value of Shipments

\$ 97.2 X 10°

	Eastern	Great Lakes <u> Gallons </u>
Intake from Public Systems	1892.5 X 109	500. X 109
Co. Surface Intake	379.6 X 109	100.3 X 109
Co. Ground Intake	(Z)	(Z)
Gross Water Used	379.6 X 109	100.3 X 109
Public Sewer Discharge	1514. X 10°	400. X 10•
Surface Water Discharge	364.5 X 109	96.3 X 109
Ground Water Discharge	378.5 X 100	100. X 10•
Transferred to cther Users	15.5 X 109	4.1 X 109
Treated before Discharge	(Z)	(Z)

Value of Shipments

\$179.8 X 10°

	Ohio	River
	<u>Liters</u>	<u> </u>
Intake from Public Systems Co. Surface Intake	378.5 X 10° 677.9 X 10°	100. X 10° 179.1 X 10°
Co. Ground Intake Gross Water Used	6.1 X 109 718.8 X 109	1.6 X 109 189.9 X 109
Public Sewer Discharge	(Z)	(Z)
Surface Water Discharge	679.4 X 109	179.5 X 109
Ground Water Discharge Transferred to other Users	757. X 106 -	200. X 106 -
Treated before Discharge	157.1 X 109	41.5 X 109

(Z) Less than 1.89 million 1/year (500,000 gal/year)

Table 8. INTAKE WATER TREATMENT PRICE TO USE: 1968

Treatment	<u>Establishments</u>	<u>109 liters</u>	<u>109 gal.</u>
Aeration	1	-	-
Coagulation	4	1.9	0.5
Filtration	4	1.5	0.4
Softening	4	. 4	0.1
Corrosion Control	4	1.5	0.5
pH	3	-	-
Other	2	-	-
None	13	-	-

Table 9. WATER TREATED PRIOR TO DISCHARGE: 1968

<u> Treatment</u>	<u>Establishments</u>	<u>109 liters</u>	<u>109 qal</u>
Primary Settling	3	-	-
Secondary Settling	3	-	-
Trickling Filters	1	-	-
Activated Sludge	2	-	-
Digestion	5	• 4	0.1
Ponds or Lagoons	6	157.5	41.6
Hq	3	-	-
Chlorination	3	-	-
Flotation	3	-	-
Other	9	-	-

PRODUCTION PROCESSES

The ferroalloy manufacturing processes are listed below with the product groups manufactured by each process.

Submerged-arc furnace process	- Silvery iron
	50% Ferrosilicon
	65-75% Ferrosilicon
	Silicon metal
	Silicon-manganese-zirconium
	High-carbon (HC) Ferro-
	manganese
	Silicomanganese
	Ferromanganese silicon
	Charge chrome
	HC ferrochromium
	Ferrochrome silicon
	Calcium carbide
Exothermic process -	Low-carbon (LC) ferro-
	chromium
	LC ferromanganese
	Medium-carbon (MC) ferro-
	manganese
	Chromium metal
	Titanium, Vanadium and
	Columbium Alloys
Electrolytic process -	Chromium metal
	Manganese metal
Vacuum furnace process -	LC ferrochromium
Induction furnace process -	Magnesium ferrosilicon
	Ferrotitanium

Ferroalloy production in submerged-arc furnaces consists of raw materials preparation and handling, smelting, and product sizing and handling as shown in Figure 1.

RAW MATERIALS PREPARATION AND HANDLING

The mineralogy of individual ores used by the ferroalloys industry is highly technical and specialized. The ores must be analyzed and carefully evaluated to identify any undesirable elements. Careful evaluation of the ore is essential not only with regard to costs, including government tariffs, since ores are commonly sold on the basis of contained metal or metallic oxide, but also with regard to freight charges to ferroalloy plants. Other considerations in the purchase of ores are their physical characteristics, ease of reduction, and analytical specifications necessary to meet customer requirements.

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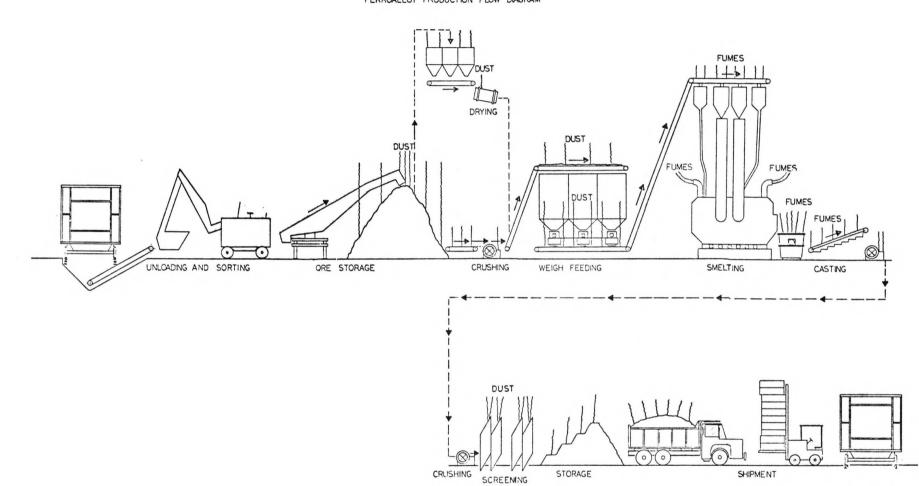


Figure 1. FERROALLOY PRODUCTION FLOW DIAGRAM

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The United States is dependent almost entirely upon commercial sources of manganese and chromium ores from cutside the country. These ores are imported mainly from South America, Africa, Turkey, India, and Russia. Since the time interval between mining the ores and their receipt at the ferroalloy plants is usually many months, or even as long as a year, a substantial stock of manganese and chromium ores of the particular types and grades necessary to produce the desired alloys must be maintained.

It is the general practice to procure ores from familiar sources since their peculiarities will be known. Such ores will have already demonstrated their suitability for the intended smelting process. There are not many known chromium ore deposits and their fundamental chemical composition and physical properties have been reasonably well defined. The same is true of commercially mined manganese ores.

Most ores come to the market for sale in the dressed state and are sold on the basis of their content of the metal oxide or metal, i.e., contained manganese, chromium oxide, etc. In general, ores containing high percentages of metal oxides are easier to process and result in lower production costs than ores with lower percentages or metal oxides.

In addition to chromium and manganese ores, columbium-bearing ores or slags, titanium ores, and zirconium cres are also imported. Commercial sources of vanadium and tungster, hearing cres exist in the United States. High-purity quartzes or quartzites with low alumina and low iron oxide are found in selected areas of this country. High quality limestone deposits are also available domestically at a few locations.

The chromium ores imported and used for ferroalloy production in the United States have a Cr203 content of about 45 to 53 percent. The manganese content of the manganese ores ranges from 43 to 54 percent. Since the ores used for ferroalloy production contain considerable gangue, ore receipts and storage at the ferroalloy plants involve large tonnages.

The sizing of ores is important. Fine ores, such as flotation concentrates, are not desirable as a direct charge into reduction furnaces because such ores lack porosity and do not allow the release of reaction gases. Dust losses are therefore high. Fine ores can be used effectively with minimum mechanical losses in melt furnaces and can later be reduced with silicon alloys. While work has been done on briquetting fine ores, equipment investment and briquetting costs have been difficult to justify through increased production and improved recovery. On the other hand, ores received at the plants are frequently oversized and must be crushed to a suitable size.

It is desirable to have in storage an adequate quantity of one with the desired chemical analysis and physical properties. The desirable quantities stored will depend on the furnace capacity, marketing situation, and storage capacity of the plant. The interest on the funds

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invested in the ores held in storage may become a significant cost factor. Often it is possible to assemble ore from several sources which will complement each other in their composition.

The ore shipment, plus the required quartzes or quartzites, lime, scrap steel turnings, and reducing agents, etc., are generally transported to plants by railway or river barges. Ores are unloaded by traveling cranes or railroad-car dumpers and moved with belt conveyors to storage areas. The free moisture in the raw materials is significant, ranging from 10 to 20 percent. In some plants, the moisture is decreased by passing the material through driers before use in furnaces.

Care is required in the preparation of furnace charges in order to produce a specified ferroalloy. Normally, raw materials are conveyed to a mix house where they are weighed and blended. After the batch has been assempled, it is moved by conveyors, buckets, skip hoist, or cars to the hoppers above the furnace, where it may flow by gravity through chutes to the furnaces.

SUBMERGED-ARC FURNACES

The general design of electric submerged-arc furnaces for the production of alloys is basically the same throughout the industry; but they differ electrical connections, arrangements of electrodes, and shape and in size of the hearth. The three carbon electrodes are arranged in a delta formation, with the tips submerged .9-1.5 m (3-5 ft.) into the charge within the furnace crucible, so the reduction center lies in the middle of the charge and the reaction gases, formed in the reduction center, pass upward through the charge. A portion of the heat is transferred to the charge and partly prereduces the ore as it passes downward into the center of the furnace. Because of the passage of the reaction gas through the charge, fume losses are reduced.

Existing submerged-arc furnaces are generally built with an open top, and large quantities of reaction gases evolved in the reaction zone during the reduction process will flow without hindrance into a hood built above the furnace. The gases burn on the surface of the charge supported by the oxygen of in-rushing air, and are then discharged through stack(s) (after gas cleaning) to the atmosphere. Due to the open configuration, the parts above the furnace, i.e., the electrode holders, the hangers, the current conductors, the charging equipment, etc., are exposed to the radiant heat of the furnace and the hot furnace gases. These components must receive effective heat protection through the use of cooling water flowing through interior passages in the metal parts. In some reduction furnaces that produce ferroalloys water-cooled covers having gas removal equipment are built over the top of the furnace crucible. In such furnaces raw materials are used that do not tend to bridge and block the flow of gas so that it is not imperative to work the charge with stoking rods. To reduce the bridging problem, raw materials may be pretreated.

The crucible of the submerged-arc furnace consists of a sealed metal shell adequately supported on foundations with provisions for cooling 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 at the top level of the bottom carbon block. In some cases, provisions are made for the furnace to rotate or oscillate slowly.

Figure 2 shows a diagram of a ferroalloy furnace while Figure 3 shows an overall cross section of the same furnace with its accessory equipment.

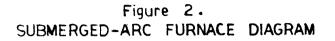
The iron content in the ferroalloy charge material and product greatly facilitates both its manufacture and use. When metals that melt at high temperatures are alloyed with iron, the resulting alloy has a lower melting temperature than the metal with the high melting point. The lower melting temperature greatly facilitates the furnace production of ferroalloys and also facilitates its solution in molten steel or iron.

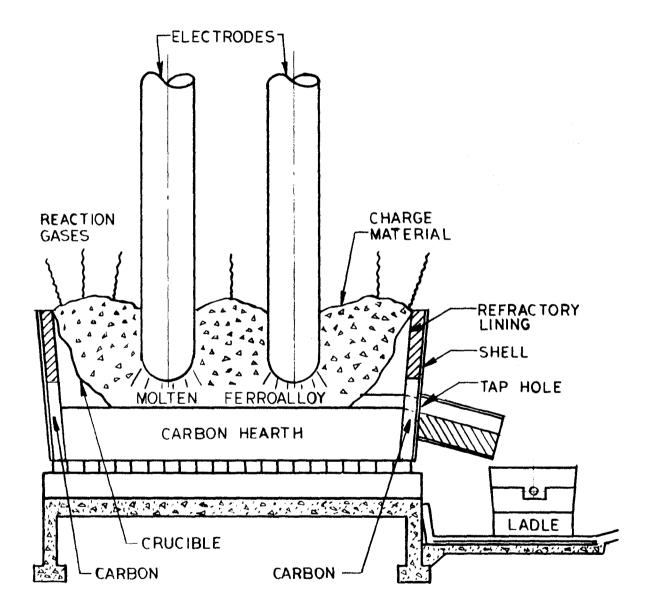
In the submerged-arc furnace the conversion of electrical energy to heat takes place by current flow from the electrode tips to the hearth and between electrodes. Final reduction of the oxidic ores occurs in the lower portion of the furnace.

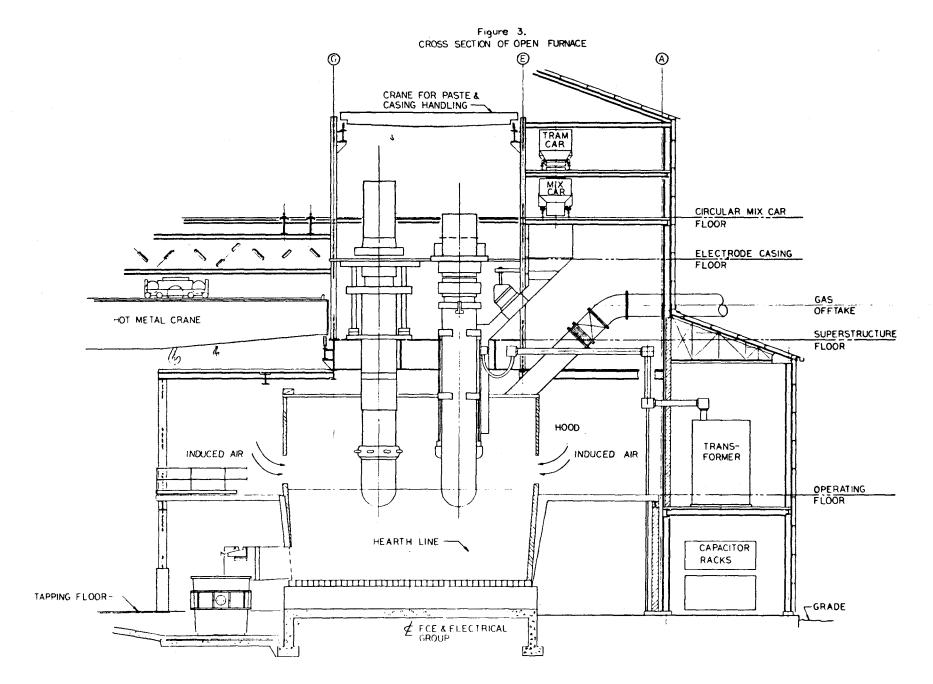
Submerged-arc furnaces generally operate continuously except for periods of power interruption or mechanical breakdown of components. Operating time averages 90 to 98 percent. The electrodes are submerged from .9 -1.5 m (3-5 ft.) below the mix level, and their tips are located about .9 -1.8 m (3-6 ft.) above the hearth. The electrodes' position thus facilitates both heat exchange and mass transfer between reaction gases and the mix.

High temperatures, up to $2000^{\circ}C$ ($3632^{\circ}F$), are required to effect reduction reactions. Carbon monoxide is a necessary byproduct of the smelting reaction. In the case of silicon metal, about 2 kg (4.4 lb) of carbon monoxide are produced for each kg (2.2 lb) of metal; significant amounts of silicon monoxide are also produced as an intermediate.

Although furnaces may be changed from production of one product group to another, such as from ferromanganese to ferrochromium, this may entail rearrangement of electrode spacing and different power loads and voltage requirements. It may also reduce the efficiency of the furnace operation, since most furnaces are designed to produce one type of alloy. However, it is relatively easy to switch from ferromanganese to silicomanganese, for example, since they are in the same product group.







The molten alloy from the carbon reduction of the ore accumulates at the base of the electrodes in the furnace. The molten alloy is periodically removed through a tap-hole placed to drain the metal from the hearth of the furnace.

FERROSILICON PRODUCTION

Quartz and quartzite are the minerals mostly used for smelting ferrosilicon. The ores should contain not less than 98 percent SiO2 and the lowest possible content of alumina, magnesium oxide, calcium oxide, and phosphorous. The reducing agent usually used is coke; other reducing agents are coal, petroleum coke, and charcoal. The reducing agent should have minimum ash and phosphorous content. The ironcontaining substance should be clean, carbon steel scrap or pelletized iron ore; the chromium and phosphorous contents should be low. These requirements preclude the use of stainless scrap and cast iron scrap.

A material balance for the production of 50% ferrosilicon is typically as shown in Table 10.

			، هم می نشد مین است هم میه خدا میک میک همی - هم میک میک میک است است میک میک است.
Input		Outpu	t
Quartzite Coke Steel Shavings	47.2 27.4 24.5	Alloy Volatilized	41.8 58.2
Electrode Mass	$\frac{c. c}{100.0}$		100.0

Table 10. MATERIAL BALANCE FOR 50% FERROSILICON (% of material charged)

The charge materials for the production of silicon metal should contain no iron. Petroleum coke or charcoal is used as the reducing agent and pre-baked carbon electrodes are generally used. Power consumption increases with increasing silicon content of the product from 50% FeSi to silicon metal.

Ferrosilicon is usually smelted in 3-phase electric furnaces which may be rated at over 40 mw. Modern ferrosilicon furnaces are equipped with continuous self-baking electrodes and automated charging machinery. The electrodes are sheet steel cylinders which are filled with the electrode paste, made of a mixture of anthracite, coke and other carbonaceous substances, and a mixture of coal tar and pitch used as a binder. The electrode is consumed during the furnace reduction process and is periodically slipped into the furnace to compensate for its consumption.

The charge materials are prepared in charge yards, transported by conveyors to the proportioning floor, and distributed among the furnace hoppers. From the hoppers the charge is fed into the furnace charge holes. During the production of ferrosilicon, the furnace operates continuously and the metal is tapped as it accumulates. Six to eight tappings per shift are made. After tapping is finished as indicated by the appearance of flame at the tap hole, plugs consisting of electrode mass or a mixture of fire clay and coke dust are rammed in.

FERROMANGANESE PRODUCTION

Electric furnaces similar to those used for the production of ferrosiliccn are used to produce ferromanganese. When ferromanganese is produced from its ores, iron, manganese, silicon, phosphorous, and sulfur are reduced and complex iron and manganese carbides are formed. Smelting is continuous with metal and/or slag being tapped every 2-4 hours.

Ferromanganese is produced in the electric furnace by either the flux The self-fluxing process is process or the self-fluxing process. In the flux process, commonly used in the United States. lime is introduced in the charge; MnO which forms silicates with the silicon in the ore and coke dust ash is displaced by calcium oxide, reducing losses of manganese to the slag. Phosphorous in the ore is mostly reduced and passes into the alloy. Up to 90% of the phosphorous in the ore can be reduced; the reduced phosphorous partially evaporates and escapes from the furnace while 60% of the total phosphorous in the charge passes into alloy. Of the total sulfur introduced in the charge 1% passes into the the alloy, 40-45% passes into the slag, and 55% escapes with the gases. The normal charge to produce high-carbon ferromanganese by the flux method is as in Table 11. The charge-to-alloy ratio is about 4.0.

Table 11. HC FERROMANGANESE CHARGE MATERIALS-FLUX METHOD (% by weight)

		جو راه خذ جدِ نذا 100 م. جو بو حد جو ای حد حالی کا حدیث این از این کا دو رو برد موجود بو مرد دو
		میں بڑک ایک چیر سی ایک میں میں 100 میں میں 200 میں میں 200 میں مالک 200 میں جو میں نہیں ہیں 200 میں میں 100 می
Manganese ord Coke Limestone Electrode mas	18.0 16.8	

In the self-fluxing method of producing ferromanganese, little or no lime is introduced in the charge; the slag is subsequently used to smelt silicomanganese. By this method, 60% of the manganese in the ore passes into the alloy, 8-10% escapes, and 30-32% passes into the slag; 70% of the manganese in the slag is extracted when silicomanganese is subsequently produced from the slag.

The normal charge to produce HC ferromanganese by the self-fluxing method is shown in Table 12. Of the charged materials, 30.9% pass into the alloy, 29.5\% pass into the slag, and 39.6% escapes as gas and dust. The gas contains 65-70% CO.

Table 12. HC FERROMANGANESE CHARGE MATERIALS -SELF-FLUXING METHOD (% by weight)

*****	هې د وار د د وې د وې د وې د وې		
Manganese Lime Coke Electrode	ore (48% Mn) mass	74.8 4.6 20.0 <u>0.6</u> 100.0	

Medium-carbon and low-carbon ferromanganese differ from high-carbon ferromanganese by their reduced carbon contents and are produced by a special process. Production in an electric furnace is usually by the silicothermic reduction method. The charge for MC ferromanganese is composed of silicomanganese, manganese ore, and lime, as shown in Table 13. The charge-to-alloy ratio is about 3.5.

Table 13. MC FERROMANGANESE CHARGE (% by weight)

Manganese ore Lime	43.6 24.3
Silicomanganese (20% Si, 65% Mn)	31.2
Electrode Mass	0.9
	100.0

A similar charge would be used to produce LC ferromanganese, but using silicomanganese with a higher silicon, lower carbon content (ferromanganese-silicon).

SILICOMANGANESE PRODUCTION

Silicomanganese is also produced in electric submerged-arc furnaces. The charge is continuously loaded and slag and metal are tapped 3 to 4 times during an 8-hour shift. Silicomanganese may be smelted from manganese ore, from self-fluxing slag from ferromanganese production, or from a combination of both.

A typical charge to produce silicomanganese is shown in Table 14.

Table 14. SILICOMANGANESE CHARGE MATERIAIS (% by weight)

والمراجعة والمراجعة والمراجعة والمراجعة والمراجعة والمراجعة والمراجع والمراجعة والمراجعة والمراجعة والمراجع		ده مها این ما میل راند ها، یک این می این این می بید ای می این این می می این ا
ىلىك مىلە كە مىلە بىرە يورە يولە خىلەرك جىن ۋەنىخىنە ئىلەرىيە جەنىپىرىدىكە _{مىل} ەرچىرىدە	یں اللہ ہے (11 مللہ می) سار سے میں اساری سر میں میں ہور میں میں میں میں میں میں ہے اور ہے اور میں خری ہیں	
Manganese Slag	27.9	
Manganese Ore	27.9	
Coal or Coke	17.3	
Lime	15.6	
Recycle Scrap	_11.3	
	100.0	

Low-phosphorous silicomanganese is produced in a manner similar to that above except that no manganese ore is used in the charge, only manganese slag.

FERROCHROMIUM FRODUCTION

Ferrochromium is produced in several grades differing mainly in carbon content. Careful selection of chrome ores is important in producing each of the several grades of alloy.

HC Ferrochromium Smelting

In the production of HC ferrochromium, the chromium and iron oxides contained in the ore are reduced by a carbonaceous reducing agent. HC ferrochromium is smelted continuously; the charge materials are fed in small portions, keeping the furnace full while metal and slag are tapped about every $1 \frac{1}{2} - 2$ hours. Smelting of HC FeCr requires higher voltages and higher power loadings than are used for most other ferroalloys.

A typical charge for the production of HC ferrochromium, normally 60-68% chromium, is shown in Table 15. The charge-to-alloy ratio is about 4.0.

Table 15. CHARGE MATERIALS FOR HC FERROCHRCMIUM (% by weight)

	الوز الك الرز، ملك مورد ومن من عنها من من اليون من اليون من اليوا من المراكة الوا الك الي الك والمراك المراك ا	بي الله عن خله الن حو الله الله عن الله
ومنتفر ويوم ومعرفاتها ويعارفني وتباري وموافقا ويعاملهم ومنافع ومعارفهم والمراجع والمراجع والمراجع والتكر	محمد الأقور بالما في الأرافين وما فقد عنه في عنه في عنه في الما في عنه في الله في الله في الله في ال	حدائد حاليدة بودائد هانه
Chromium ore	72.4	
Coke	14.7	
Quartzite	6.6	
Bauxite flux	5.5	
Electrode mass	8	
	100.0	

The charge elements pass into the smelting products as shown in Table 16.

	%	in total	charge
Element	to alloy	<u>to`slàg</u>	<u>loss</u>
hromium	90	6	4
con	98	2	-
licon	15	80	5
nosphorous	60	20	20
ilfur	10	30	60

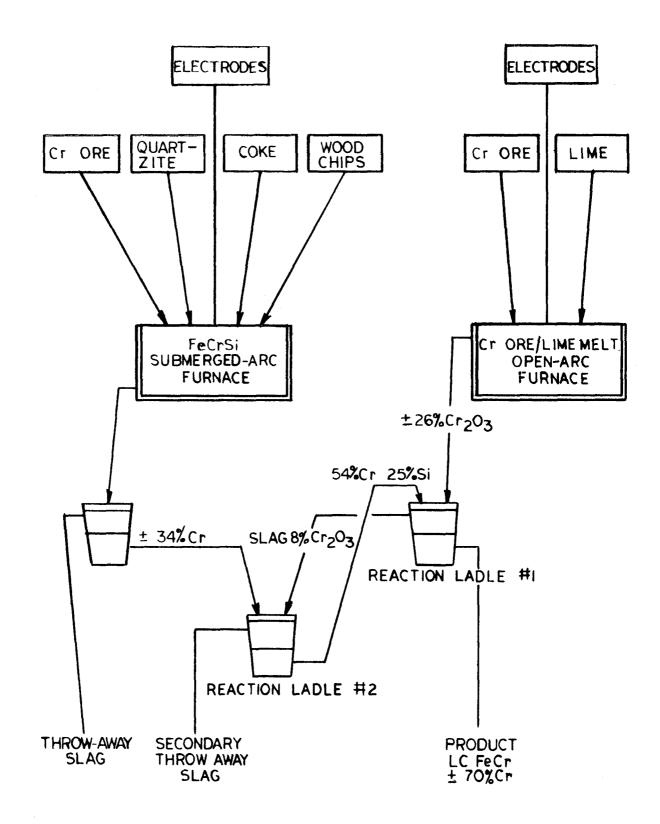
Table 16. RAW MATERIAL COMPONENTS TO SMELTING PRODUCTS FOR HC FeCr

Ferrochromesilicon Smelting

Ferrochromesilicon is generally produced by the direct method. In the direct method, chromium ore and quartzite are reduced by coke. The process is carried out in arc furnaces similar to those used in the production of ferrosilicon.

EXOTHERMIC PROCESSES

The exothermic process using silicon or aluminum, or a combination of the two, is used to a lesser extent than the submerged-arc process. In the exothermic process the silicon or aluminum combines with oxygen of the charge, generating considerable heat and creating temperatures of several thousand degrees in the reaction vessel. The exothermic process is generally used to produce higher grade alloys with low carbon content. Low-carbon and medium-carbon ferrochromium and low-carbon or medium-carbon ferromanganese are produced by silicon reduction. A flow diagram of a typical silicon reduction process for manufacturing LC ferrochromium is shown in Figure 4. First, chromium ore and lime are fused together in a furnace to form a chromium ore/lime melt. Second, a known amount of the melt is poured into the No. 1 reaction ladle followed by a known quantity of an intermediate molten ferrochromesilicon previously produced in a No. 2 ladle. The reaction in the No. 1 ladle is a rapid reduction of the chrome from its oxide and the formation of LC ferrochromium and a calcium silicate slag.



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Since the slag from ladle No. 1 still contains recoverable chromium oxide, a second silicon reduction is made in the No. 2 ladle with molten ferrochromesilicon directly from the submerged-arc furnace. The reaction in the No. 2 ladle produces the intermediate ferrochromesilicon used in the No. 1 ladle reaction. LC and MC ferromanganese are produced by a similar practice using a silicon bearing manganese alloy for reduction.

The reaction in these ladles from the silicon reduction results in a strong agitation of the molten bath and a rise in temperature. The elevated temperature and agitaticn produces emissions for about five minutes per heat that have similar characteristics to the emissions from submerged-arc furnaces.

ALUMINUM REDUCTION

Aluminum reduction is used to produce chromium metal, ferrotitanium, ferrovanadium and ferrocolumbium. Although aluminum is a more expensive reductant than carbon or silicon, the products are purer. Mixed aluminothermal-silicothermal processing is used for the production of ferromolybdenum and ferrotungsten. Usually such alloys are produced by exothermic reactions initiated by an external heat source and carried out in open vessels. The high-temperature reaction of aluminum reduction produces emissions for a limited time similar to those by silicon reduction.

SLAG PROCESSING

Some of the electric-arc smelting processes produce slag along with the ferroalloy product. These are:

Low-carbon Ferrochromesilicon High-carbon Ferrochromium High-carbon Ferromanganese Silicomanganese

These slags may contain metal entrapped in the slag which is recovered by crushing and separation of the slag and metal by a wet sink-float process, called slag concentration. The slag fines are also separated from the heavier particles so that a secondary product is slag of such size that it is usable for road building and similar purposes. This process is usually applied to ferrochromium slags for recovery of chromium which is re-charged to the furnace.

Another method of recovering metal values from manganese slag is to "shot" the slag, then use the slag as the raw material for electrolytic production of the metal. Rapid quenching of the molten slag in a large volume of flowing water produces a small-sized particle (shot) which can be readily leached with acid to produce the electrolyte solution for electrolytic manganese production.

VACUUM AND INDUCTION FURNACE PROCESSES

The vacuum furnace process for producing LC ferrochromium was developed commercially in the early 1950's. In this method, carbon is removed from HC ferrochromium in a solid state within vacuum furnaces carefully controlled at a temperature near the melting point of the alloy. Such a furnace is shown in Figure 5.

The process is based on the oxidation of HC ferrochromium by the oxygen in silica or chrome oxide, with which it has been mixed after crushing. The CO gas resulting from the reaction is pumped out of the furnace in order to maintain a high vacuum and to facilitate the ferrochromium decarburization. Heat is supplied to the furnace by electric resistance elements.

Induction furnaces, either low-frequency or high-frequency, are used to produce small tonnages of a few specialty alloys through remelting of the required constituents. Such a furnace is shown in Figure 6.

PRODUCT SIZING AND HANDLING

Ferroalloys are marketed in a bread range of sizes from pieces weighing 34.1 kg (75 lbs.) to granules of 100 mesh or finer, depending upon the final usage. Ferroalloys are intermediate products, and are usually melted and blended with molten metal. For this reason, the ferroalloy product size is important.

Molten ferroalloys from the submerged-arc furnaces are generally tapped into refractory-lined ladles and then into molds or chills for cooling. The chills are low, flat iron or steel pans that remove heat rapidly from the molten pour. After the ferroalloy has cooled to a workable temperature, it is cleaned of any adhering slag and sized to market specifications.

The sizing operation consists of breaking the large initial chills by drop weights or hammers, then crushing and screening the broken product. Large jaw crushers, rolls, mills, or grinders for reducing the product size and rotating and vibrating screens are used for this purpose. Conveyors and elevators move the product between the crushing and screening operations. Storage bins are provided to hold the finished or intermediate products.

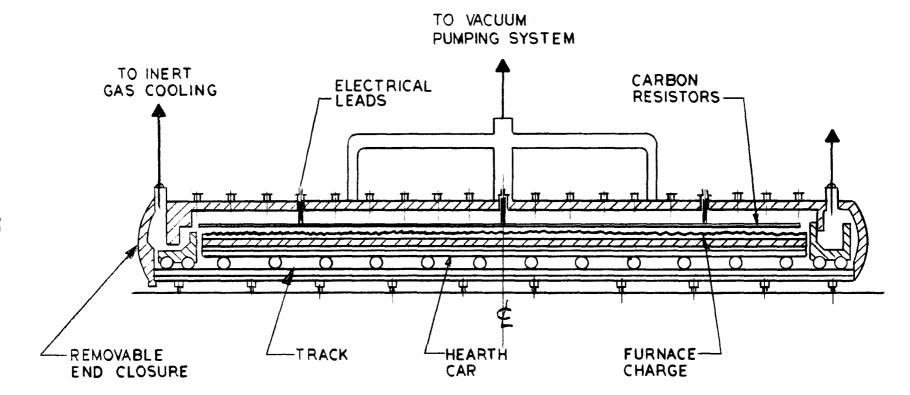


Figure 5. VACUUM FURNACE FOR FERROALLOY PRODUCTION

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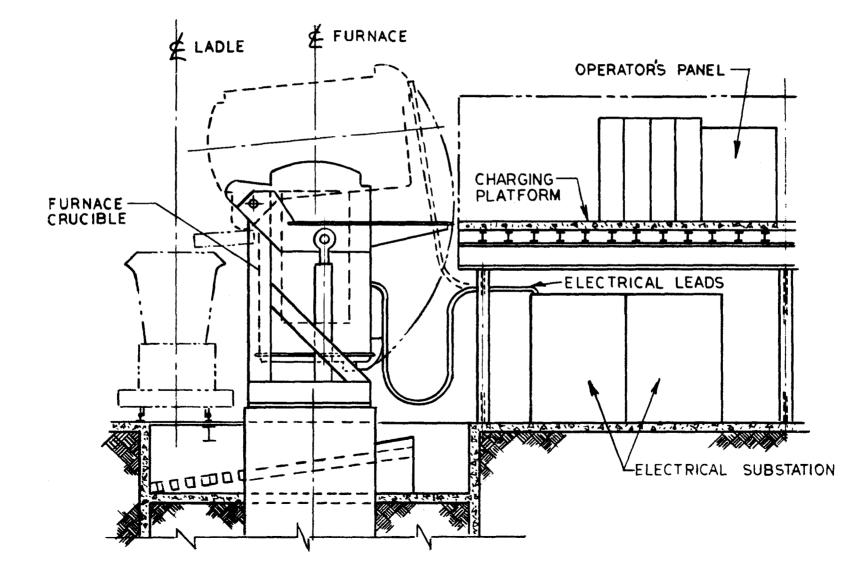


Figure 6. INDUCTION FURNACE DIAGRAM

EMISSIONS FROM SUBMERGED-ARC FURNACES

Since the quantity and composition of the emissions from ferroalloy furnaces 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 conventional submerged-arc furnace utilizes carbon reduction of metallics in the oxide ores, and continuously produces large quantities of hot carbon monoxide which can be greater by weight than the metallic product. The CO gas venting from the top of the furnace carries fume 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.

Properties and quantities of emitted particulates depend upon the alloy being produced. Except for ejected mix particles from the furnace the fume size is generally below two microns (u) and ranges from 0.1 to 1.0u with a geometric mean of 0.3 to 0.6 depending upon the ferroalloy produced. In some cases, agglomeration does occur, and the effective particle size may be larger. Grain loadings and flowrates are dependent upon the type of furnace and hooding. Open submerged-arc furnaces have high flowrates and moderate grain loadings, while covered furnaces have moderate flowrates and generally high grain loadings. In the dry state, the collected emissions are very light and the bulk density varies from 64.1 to 480.6 kgs./cu. meter (4 to 30 pounds per cubic foot).

Silicon alloys produce a gray fume containing a high percentage of primarily amorphous silicon dioxide (SiO2) (Ref. 5). Some tars and carbon are present arising from the coal, coke, or wood chips used in the charge. Ferrochrome-silicon furnaces produce an SiO2 emission similar to a ferrosilicon operation with some additional chromium oxides. Manganese operations produce a brown emission, which analyses indicate to be largely a mixture of SiO2 and manganese oxides. The emissions from chromium furnaces contain SiO2, MgO and some iron and chromium oxides.

Chemical analysis of the fumes indicate their composition to be similar to oxides of the product being produced. Typical chemical analyses are given in Table 17.

							Chrome ore-	- Mn ore-
Furnace product	50% FeSi	SMZ a	SiMn ^b	SiMn ^b	FeMn	HC FeCr	<u>lime melt</u>	<u>lime mel</u>
Furnace type Fume shape	Open Spherical,	Open Spherical.	Covered Spherical	Covered Spherical	Open Spherical	Covered Spherical	Open Spherical	Open Spherical
	sometimes in chains	sometimes in chains	ophorizour	opnorizeur	opherical	ophorizour	and irregular	and irregular
Fume size char-							8	8
acteristics,								
microns								
Maximum	0.75	0.8	0.75	0.75	0.75	1.0	0.50	2.0
Most particles	0.05 to 0.3	0.05 to 0.3	0.2 to 0.4	0.2 to 0.4	0.05 to 0.4	0.1 to 0.4	0.05 to 0.2	0.2 to 0.
X-ray diffraction								
				marily amorp		- · -		
trace constituents		Fe304	Mn 304	Quartz	Mn 304	Spinel	Spinel	Ca0
	FeSi2	Fe ₂ 03	MnO	SiMn	MnO	Quartz		
		Quartz SiC	Quartz	Spinel	Quartz			
Chemical								
Analys is, %								
S102	63 to 88 ³	61.12	15.68	24.60	25.48	20.96	10.86	3.28
FeO		14.08	6.75	4.60	5.96	10.92	7.48	1.22
MgO		1.08	1.12	3.78	1.03	15.41	7.43	0.96
CaO		1.01	-	1.58	2.24	-	15.06	34.24
MnO		6.12	31.35	31.52	33.60	2.84	-	12.34
A1203		2.10	5.55	4.48	8.38	7.12	4.88	1.36
LOI		-	23.25	12.04	-	-	13.86	11.92
TCr as Cr ₂ O ₃		-	-	-	-	29.27	14.69	-
SIC		1.82	-	-	-	-	-	-
ZrO ₂		1.26		-		-	-	-
РЬО		-	· 0.47	-	-	-	-	0.98
Na20		-	-	2.12	-	-	1.70	2.05
BaO		-	_	-	-	-	-	1.13
K ₂ O				-		_		13.08

Ref. 5 Table 17. TYPICAL FURNACE FUME CHARACTERISTICS

a Si - 60 to 65%; Mn - 5 to 7%; Zr - 5 to 7% b

Manganese fume analyses in particular are subject to wide variations, depending on the ores used.

EMISSIONS FROM EXOTHERMIC PROCESSES

Oxide fumes similar in physical characteristics to those from the submerged-arc furnace are emitted from the reaction ladle or furnace while the reducing agent is being charged during alumino- or silicothermic reduction. This emission is due to strong agitation of the molten bath and the rapid temperature rise. The reaction may take from 5-15 minutes per heat, and the heat cycle is about 1 1/2 to 2 hours. Therefore, atmospheric emissions from the exothermic reactions take place during about 10 percent of the cycle.

The quantity of emissions from the exothermic reactions ranges from 9.08 to 18.6 kg (20-40 lbs) of particulates per ton of ferroalloys produced. The total tonnage of ferroalloys made by the exothermic process amounts to 10 to 15 percent of the total ferroalloys production in the United States.

OPERATING VARIABLES AFFECTING EMISSIONS

Because of the complexity of the heavy mechanical and electrical equipment associated with a modern submerged-arc furnace, close supervision and maintenance are required to prevent frequent furnace shutdowns. The furnaces are designed to operate continuously to maintain satisfactory metallurgical and thermal equilibria.

Normal furnace shutdowns on an annual basis may average three to ten percent of the operating time and are caused by a wide variety of situations. These can be electrode installations, maintenance, repair of water leaks at electrode contact plates, mix chute failures, furnace hood or cover failures, taphole problems, electrical or other utility failures, crane failures, ladle or chill problems or curtailments of service by the power companies. In general, furnace interruptions are relatively short in duration and usually are not more than several hours. Following such interruptions, the furnace usually returns to normal operation with normal emissions in a period of time approximately equal to the length of the interruption.

Greater-than-normal emissions occur after returning power to the furnace following a lengthy interruption caused by a major furnace operational problem. These problems may include electrode failure that makes it necessary to dig out an electrode stub or to bake at a reduced load for self-baking electrodes, serious mixture blows of the furnace, metallurgical problems that require a furnace burndown to return it to normal operations, serious water leaks that flood the furnace with water, furnace hearth failure, major taphole problems, transformer or major electrical system failures, etc. When starting up a new furnace or one with a cleaned out hearth, as well as a furnace with a cold hearth after a long shutdown, heavier-than-normal emissions may last up to a week before the furnace operates in an optimum manner. The quantity of emissions from 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.

QUANTITIES OF EMISSIONS

Emissions and emission rates will vary with (1) type of alloy produced, (2) process (i.e., continuous or batch), (3) choice of raw materials and pretreatment thereof, (4) operating techniques, (5) furnace size, (6) maintenance practices.

An example of the varying emissions that result from process changes can be seen in the manufacturing of silicon alloys. As the percentage of silicon in the alloy increases, the loss of SiO2 increases, therefore, a silicon-metal furnace emits substantially more SiO2 fumes than an equivalent-size 50% ferrosilicon furnace.

Emissions from batch-operated open-arc furnaces are periodic. Following sudden addition of mix containing volatile or reactive constituents (coal, moisture, aluminum, etc.) to a hot furnace crucible, violent gas eruptions can occur. This is best exemplified by the manganese ore-lime melt furnace where momentary gas flow following mix addition can be five times the average flow. Under these conditions, temperature, dust loading, and gas flow all peak simultaneously. In contrast, chromium ore-lime melt furnaces, to which few or no gas-releasing constituents are fed, are not subject to this violent behavior.

Some of the special alloys are also produced by aluminothermic reactions without the addition of electrical energy. These reactions also cause momentary peaks of gas flow with high emission rates.

Volatile materials in the furnace charge may cause rough operation. One significant contributor to such operation is the presence of fines, dense material These materials promote moisture or in the feed. bridging and nonuniform descent of the charge which may cause gas channels to develop. The collapse of a bridge causes a momentary burst A porous charge will promote uniform gas distribution and of gases. decrease bridging. For some products economics dictates the use of raw materials with more fines or with more volatile matter than desirable. Pretreatment of the feed materials promotes smooth furnace operation. Each of these factors has an effect on the smooth operation of the furnace, and consequently upon the emissions.

Differences in operation techniques can have a significant effect on emissions. The average rate of furnace gas production is directly proportional to electrical input, so that a higher load on a given furnace normally causes a proportional increase in emissions. In some cases, emissions increase at a rate greater than the load increase, due to rough operation and inadequate gas withdrawal. At a fixed load and with the gas generation remaining almost constant, the emission concentration and weight per hour of particulates can vary by a factor of 5 to 1. Operating with insufficient electrode immersion promotes increased emissions.

Higher voltage operation for a given furnace will promote higher electrode positions and increase the concentration and amount of emissions.

On some operations, especially silicon metal production, the charge must be stoked to break up crusts, cover areas of gas blows, and permit the flow of reaction gases. Therefore, both furnace operations and emissions can be a function of how well and how often the furnace is stoked.

Maintenance practices significantly affect emissions on covered furnaces because accumulation of material under the cover and in gas ducts reduces the gas withdrawal capacity of the exhaust system. Plugging of gas passages in the control equipment results in reduced efficiency of gas cleaning.

PRODUCTION AND EMISSION DATA FOR FERROALLOY FURNACES

The data in Table 18 summarize pertinent data as to production and emission factors for submerged-arc furnaces (Ref. 32).

The data of Table 19 summarize the types of air pollution control devices used in various ferroalloy furnaces producing specific products in the United States.

Some comparisons of the off-gas volume from covered furnaces and controlled open furnaces are shown in Table 20.

Table 20. ILLUSTRATIVE OFF-GAS VOLUMES FROM OPEN AND CLOSED FURNACES - REF 32.

	ي بين من			
	Closed	Furnaces	Open Furnac	es
Product	<u>Nm³/min-mw</u>	<u>scfm/mw</u>	<u>Nm³/min-mw</u>	<u>scfm/mw</u>
FeMn	6.16	220	370	13,200
FeSi (65-75%)	5,88	210	521	18,600
SiMn	5.60	200	204	7,300
FeSi (50%)	5.04	180	258	9,200

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Product	<u>Uncontrol</u> kg/kkg_alloy	led Particulate			Electric <u>mwhr/kkg_alloy</u>		Ratio of Charge to Product Weigh
Silvery Iron	58	116	20.4	45	2.9	2.6	1.8
50 % FeSi	223	446	40.4	89	5.5	5.0	2.5
65-75% FeSi	458	915	47.2	104	9.7	8.8	4.5
Si Metal	500-1000	1000-2000	33-65	72-144	15.4	14.0	4.9
SMZ	No data	No data			9.7	8.8	4.5
Mn ore/lime melt	67	133	37.7	83	1.8	1.6	3.5
CaSi	672	1343	51.7	114	13.0	11.8	3.9
HCFeMn	168	335	28.1	62	2.6	2.4	3.0
SiMn	110	219	22.7	50	4.9	4.4	3.1
FeMnSi	158	315	26.3	58	6.0	5.4	4.3
FeCrSi	416	831	50.8	112	8.2	7.4	3.4
Chg Cr	168	335	28.1	62	4.6	4.2	4.0
HCFeCr	168	335	28.1	62	4.6	4.2	4.0
Cr ore/lime melt	6	11	4.1	9	1.3	1.2	1.2

Table 18. PRODUCTION AND EMISSION DATA FOR FERROALLOY FURNACES

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Table 19. TYPES OF AIR POLLUTION CONTROL SYSTEMS USED ON AMERICAN FERROALLOY FURNACES

Covered furnaces with withdrawal and cleaning of unburned gases		Open furnaces with withdrawal and cleaning of burned gases		
Control device	Products	Control device	Products	
Wet scrubbers	Ferromanganese 50 to 75% Ferrosilicon	Wet scrubbers	50 to 85% Ferrosilicon Silicomanganese HC ferrochromium	
	HC ferrochromium Silicomanganese	Cloth type filters	Ferrochrome-silicon Silicomanganese Ferromanganese silicon 75% and higher grades of ferrosilicon Silicon metal	
		Electrostatic precipitator	Ferrochromesilicon HC ferrochromium Ferrochromesilicon	

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SECTION IV

INDUSTRY CATEGORIZATION

The purpose of the effluent limitation guidelines can be realized only by categorizing the industry into the minimum number of groups for which separate effluent limitation guidelines and new sources performance standards must be developed. The categorization here is believed to be that minimum, i.e., the least number of groups having significantly different water pollution potentials and treatment problems.

- I. Open Electric Furnaces with Wet Air Pollution Control Devices
- II. Covered Electric Furnaces and Other Smelting
- Operations with Wet Air Pollution Control Devices
- III. Slag Processing

In developing the above categorization, the following factors were considered as possibly providing some basis for categorization. These factors include characteristics of individual plants, various production processes, and water uses.

- 1. Air Pollution Control Equipment
- 2. Production Processes
 - a. Electric Furnace
 - b. Exothermic
 - c. Slag Processing
- 3. Furnace Types
 - a. Open
 - b. Covered or Sealed
- 4. Raw Materials
- 5. Product Produced
- 6. Size and Age of Production Facilities
- 7. Waste Water Constituents
- 8. Treatability of Wastes
- 9. Water Uses

- a. Wet Air Pollution Control Devices
- b. Cooling Water
- c. Electric Power Generation
- d. Sanitary Wastes
- e. Slag Processing
- f. Drainage From Slag or Raw Material Storage

Air Pollution Control Equipment

Air pollution is the major pollution problem in this industry. Much of the water pollution problem is created by solving air pollution problems with wet air pollution control devices such as scrubbers. Since the only water pollution potential from an electric furnace, which is either uncontrolled or controlled with a dry air pollution control system (such as a baghouse), is that from cooling water, there is no justification including these furnaces with those having wet systems, since any for standard which would be fair to the 'wet' furnaces, would be excessively permissive to the 'dry' ones, and vice versa. For this reason, the categorization selected is partially based upon the type of air pollution control equipment, i.e., wet or dry.

Although another breakdown might be made based upon the types of wet air pollution control equipment, such as high energy scrubbers, disintegrator scrubbers, electrostatic precipitators with water sprays, etc., this would unnecessarily multiply the number of categories and have too small an effect upon the total pollutant load from this industry to be warranted.

Production Processes

The various production processes vary markedly in their ability to pollute water, and this provides an additional basis for categorization. loads This basis consists of the differential in raw waste and concentrations between the slag processing operations and the electric furnace and exothermic processes. The electric furnace and exothermic processes are dry by nature, although water is used for cooling and possibly for air pollution abatement. The plant survey data obtained at an exothermic operation using wet air pollution control methods indicate that the water use per ton (when divided by 3) is of the same order of magnitude as that of covered electric furnaces (per mwhr), and the exothermic operations were therefore included with the covered electric furnaces.

Although not properly a ferroalloy production process, slag processing is performed at many plants to recover the residual metal values left in the slag after smelting, and helps reduce the solid waste load somewhat at these plants. This process is intrinsically different from the other production processes, inasmuch as it is inherently 'wet', and therefore merits a separate category. Additionally, the 'building block' approach, such as is used for establishing the allowable plant effluents herein, requires a separate category since all plants dc not use such a process and the magnitude of the potential wasteload is substantial.

Furnace Types

The types of smelting furnaces were found to provide a basis for categorization in conjunction with consideration of water uses and other factors. The differences between open and covered or sealed electric smelting furnaces are significant insofar as they relate to the raw waste loads and the pollutants present and air pollution control technologies available for use. The off-gas volumes from the two types of furnaces may vary by a factor of 50 between the two types of furnaces, and cyanides are present in scrubber waters from the covered types, but not from the open type. The water uses for wet air pollution control devices may be quite different due to the differences in the off-gas volumes. Person's (5) published data show a difference in water circulation with venturi scrubbers of a factor of 24 between open and covered furnaces. The final volume of water flowing from the scrubbers on open or covered furnaces may not vary significantly; the plant survey data indicate, in fact, that the differences are not great and are probably more dependent on scrubber type than furnace type. The recirculation of water at the venturi scrubbers on open furnaces must be regarded as a part of the waste water treatment methods and is so specified when effluent limitations for such sources are determined.

Additionally, dry dust collectors are widely used on open furnaces, and are more common than wet collectors. The converse is true with covered furnaces. There are only two known examples of dry dust collectors being installed on covered or sealed furnaces, while the vast majority utilize wet air pollution controls.

<u>Raw_Materials</u>

Depending on the product produced, the raw materials for the smelting operations vary principally in the types of ores and the proportions of the materials in the charge. For example, the charge for HC ferromanganese consists of manganese ore, coke, and limestone, while the charge for HC ferrochromium consists of chromium ore, coke, quartzite and hauxite flux. There are no differences, however, in the raw materials used in the production of 50% ferrosilicon, whether it is produced in an open or covered furnace, although the covered furnace feed materials may require pretreatment. There are, of course, substantial differences in the charge into electric furnaces and the feed to slag processing operations.

Product Produced

Categorization by product would result in a large number of guidelines and standards, since the number of products which can be produced in a furnace is fairly large, and many products can be produced in either open or covered furnaces. Additionally, this method would create unnecessary problems for the person writing the discharge permit, since plants are accustomed to changing the product produced in the furnaces depending upon market conditions. For example, during the last few years, with a decline in the market for ferrochromium and ferromanganese products, many plants discontinued or cut back the product lines. With a categorization based on product, this would either entail the issuance of a new discharge permit, or the writing of the original permit to reflect all the possible variations which may take place.

Size and Age of Facilities

The size and age of production facilities provides no basis for categorization. This judgement is based largely upon the fact that the emissions factors for the various products (given in kg (lb)/mwhr and which represent the uncontrolled particulate emissions and upon which the raw waste water loads are dependent) are not variable by furnace size. Since effluent loads were based upon units of electric power used in the furnaces, the factor of furnace size seems to be eliminated by the nature of the process. Size of the plant may have some bearing on the cost of waste water treatment, since obviously it will cost a very small plant more for treatment per unit capacity than it would a large one, but this is not so great as to warrant a separate categorization.

Although clder furnaces are not as likely to be controlled for air emissions, and therefore to require scrubber water treatment, by the nature of the categorization selected this has been taken into account. The newer electric furnaces differ from the older ones only in size; the older furnaces are about 10 mw or less, the newer ones are double or triple that in size. The essential nature of the furnace has changed little over many years, although newer furnaces may utilize somewhat more water for cooling.

Waste Water Constituents

The waste water constituents provide a collateral, but not independent basis for categorization. Suspended solids are the largest single constituent of the waste waters and appear in effluent from all of the various processes. Suspended solids cbviously result from the use of wet devices to remove particulates from smelting off-gases. Chromium, as another example, is in the effluents from chromium smelting operations, and chromium slag concentrating operations. Cyanides are generated in significant concentrations only in covered furnaces. This distinction appears in the differentiation between open and closed furnaces and is thus no independent basis for categorization based on waste water constituents.

Treatability of Wastes

Treatability of waste also provides a collateral, but not independent basis for categorization, largely for the same reasons that the waste constituents do. The treatment methods consist principally of precipitation, coagulation and sedimentation, neutralization and of cyanides and phenol, and of chromium, oxidation reduction these methods, except for cyanide recirculation and re-use. All of oxidation, are applicable to one extent or another in all of the various in significant types of production operations. Cyanide is found quantities only in scrubber water from covered furnaces, but such a differentiation is inherent in the chosen categorization, since covered furnaces are separately considered for other reasons.

From the standpoint of air pollution control, emissions from open electric furnaces are fairly easily controlled with fabric filter systems, and this method has been commonly used in the industry for this type furnace. Covered or sealed furnaces, however, in this country are only controlled with wet scrubbers, although there are two foreign plants which utilize dry dust collection systems for control of emissions from covered furnaces.

The use of baghouses, of course, reduces water use to zero insofar as air pollution controls are concerned, and a smelting furnace shop so equipped does not fall under the categories based upon furnace type.

Water Uses

Water uses were judged to be a significant basis for categorization. The categorization differentiates between processes on the basis of water use for wet air pollution control devices and for slag processing.

Electric power is presently generated in very few ferroalloy plants. A separate category is not warranted; the guidelines separately developed for steam electric power plants should be applicable, since, as shown in the previous section, water use per kwhr is about the same as for power plants in general. Sanitary wastes are common to all plants, whether treated on-site or discharged to a municipal treatment plant and no separate category is needed.

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SECTION V

WASTE CHARACTERIZATION

The waste characteristics to be determined may be considered on the basis of the industry categories and the various water uses as follows:

- 1. Water for Wet Air Pollution Control Devices
 - a. Electric Furnace Smelting
 - i. Disintegrator-type Scrubbers
 - ii. High Energy Scrubbers
 - iii. Electrostatic Precipitator Spray Towers
 - iv. Steam/Hot Water Scrubbers
 - Exothermic Smelting Processes
- 2. Sanitary Uses, Boiler Feed, Air Conditioning, etc.
- 3. Slag Processing Uses

b.

PUBLISHED DATA SOURCE CHARACTERIZATIONS

A total of 2,329,630 kkgs (2,568,500 tons) of ferroalloys were produced in 1967, using 11,206 million kw-hrs. of electric energy according to the <u>1967 Census of Manufactures</u> Of the total energy used, 3,354 million kw-hrs. were generated by ferroalloy plants. Assuming miscellaneous losses and other uses of 15 percent, an average use of 4,089 kw-hrs. per kkg (3,709 kw-hrs. per ton of alloy in terms of furnace power is indicated.

Total water intake for S.I.C. 3313 plants was 1128.7 X 10° liters (298.2 X 10° gals.) per year according to the <u>1967 Census of Manufactures</u> while gross water use was 1212.3 X 10° liters (320.3 X 10° gals.). Intake for cooling was 381.5 X 10° liters (100.8 X 10° gals.). Assuming that all water recirculation and reuse was for cooling, cooling water use was 465.2 X 10° liters (122.9 X 10° gals.) Cooling water use of 199,679 liters per kkg (47,849 gal. per short ton) of alloy, or 48.8 liters (12.9 gals.) per kw-hrs. of furnace power is indicated.

The <u>1967 Census of Manufactures</u> indicates a water use of 701.4 X 109 liters (185.3 X 109 gals.) of water in generating the aforementioned 3,354 million kw-hrs. of electric energy in-plant. The indicated use of 208.9 liters (55.2 gals.) per kw-hrs. is about equal to the 1964 thermal electric power plant use of 215 liters (56.8 gals.) per kw-hr. (Final Report, EPA Contract 68-01-0196). Assuming losses and other uses at 15 percent, a water use of 245.6 liters (64.9 gals.) per kw-hr. of furnace power is indicated for in-plant power generation.

The 1967 census data indicate a use of 40.9 X 109 liters (10.8 X 109 gal.) per year for sanitary, boiler feed, air conditioning, and other minor uses and plant employment of 8,700. At 378.5 liters (100 gals.) per capita per day, 250 days per employee per year, sanitary use would have been 825 X 106 liters (218 X 106 gals.) per year; air conditioning

use was 757 X 10⁶ liters (200 X 10⁶ gals.) per year. These uses total 4.28 liters (1.13 gals.) per kw-hr. of furnace power, assuming losses and other uses at 15 percent.

Person's data (5) indicate the water use in high energy scrubbers on open furnaces as 113.6 1/sec (1,800 gpm) for each of three furnaces producing FeCrSi, SiMn, and HC FeCr and rated at 25, 30 and 30 mw, respectively. At an assumed operating load of 75% with 95% operating time, the indicated water use is 1,226,340 liters (324,000 gals.) per 60.6 mw-hrs., or 20,238 liters (5,347 gals.) per mw-hr. of furnace power.

Person's data further indicated an average use of 5.5 l/sec (87.5 gpm) for a high energy scrubber on a semi-closed 45 mw 50% FeSi furnace. At 95% operating time and 75% operating load, the indicated water use is 620.7 liters (164 gals.) per mw-hr. of furnace power.

According to Retelsdorf, et.al. (6) an electrostatic precipitator installed on a 20 mw ferrochromesilicon furnace uses water in a spray tower preceeding the precipitator at the rate of about 9,084 liters (2,400 gals.) per hour. This indicates a use of 635.9 liters (168 gals.) per mw-hr. of furnace power at 95% operating time and 75% operating load. About 10-15 % of the water used is discharged from the bottom of the spray tower, the remainder being evaporated into the gas stream. These data indicate about 556.4 liters (147 gals.) of water per mw-hr. of furnace power evaporated in the gas stream.

From the above data and those given in Section III, some limited calculations of waste characteristics may be made.

Assuming that 556 liters (147 gals.) of water per mw-hr. of furnace power is evaporated in the gas streams from open furnaces using wet air pollution control devices and that such evaporation in the case of covered furnaces is in proportion to the gas volume, the effluent volumes expected would be as follows:

High energy scrubbers (open furnace) = 19,682 1/mw-hr (5200 gal/mw-hr)

High energy scrubbers (covered furnace) = 609 1/mw-hr (161 gal/ mw-hr)

Electrostatic precipitator = 79.5 1/mw-hr (21 gal/mw-hr)

On the basis of the data given in Section III on production processes, compositions of raw materials, and compositions of products and byproducts, the following constituents/parameters appear to be those potentially present in waste water:

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Acidity	Columbium	Potassium
Alkalinity	Cyanide	Radioactivity
Aluminum	Dissolved Solids	Silica
Ammonia	Iron	Sulfates
Barium	Magnesium	Suspended Solids
B. O. D.	Manganese	Temperature
Calcium	Molybdenum	Titanium
Chromates	Hq	Vanadium
Chromium	Phosphates	Zirconium

WASTE CHARACTERIZATIONS FROM DISCHARGE PERMIT DATA

Waste constituents/parameters listed as present in discharge permit applications for the plants in S.I.C. 3313 are as follows:

Algicides	Fluorides	Sodium
Aluminum	Hardness	Solids
Ammonia	Iron	Sulfate
Barium	Magnesium	Sulfide
Boron	Manganese	Sulfite
Calcium	Nickel	Surfactants
Chloride	Nitrate	Titanium
Chromium	Oil and Grease	Turbidity
Color	Organic N	Zinc
Copper	Phosphorous	

Additionally, pH and temperature are given as waste parameters.

WASTE CHARACTERIZATIONS FROM PLANT SURVEY DATA

Waste characteristics were determined where possible from the plant survey data for various specific waste-producing sources. These data, of course, apply to the particular units operating as they were during the sampling period and represent the type of result to be expected during the actual operation. To the extent possible, reasons for variations are explained.

WASTE CHARACTERIZATION - OPEN ELECTRIC FURNACES WITH WET AIR POLLUTION CONTROL DEVICES

The data from Plant D provides raw waste loads for open submerged arc furnaces in which the off-gases are scrubbed with steam/hot water scrubbers as shown in Table 21.

Table 21. RAW WASTE LOADS-OPEN CHROMIUM ALLOY AND FERROSILICON FURNACES WITH STEAM/HOT WATER SCRUBBERS

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<u>Constituent</u> Suspended Solids	kg/mwhr	<u>lbs/mwhr</u>
Suspended Solids	8.2	18.1
Manganese	.005	0.010
Cr, total	.003	0.007
Cr, hex.	.002	0.004
	<u>l/mwhr</u>	gals/mwhr
Flow	2,691	711

The data from Plant E provide an additional raw waste load for an open electric furnace using a venturi scrubber, as shown in Table 22.

Table 22. RAW WASTE LOAD - HIGH ENERGY SCRUBBER ON OPEN ELECTRIC FURNACE

Constituent	<u>kq/mwhr</u>	<u>lb/mwhr</u>	
Suspended Solids	23.74	52.29	
Manganese	10.06	22.15	
Chromium (Total)	0.002	0.005	
	<u>l/mwhr</u>	<u>gals/mwhr</u>	:
Flow	6,382	1,686	

The data from Plant G providing raw waste loads for open submerged arc furnaces in which the off-gases are conditioned in a spray tower preceding an electrostatic precipitator are shown in Table 23.

Constituent	<u>kg/mwhr</u>	<u>lbs/mwhr</u>
Suspended Solids Manganese Chromium, total	.289 .0012 .0016	0.636 0.0026 0.0036
	1/mwhr	<u>gals/mwhr</u>
Flow	84.0	22.2

Table 23. RAW WASTE LOADS-OPEN CHROMIUM ALLOY FURNACES WITH ELECTROSTATIC PRECIPITATORS

Although the data as given in Table 23 for water flow agrees quite well with that predicted (84.0 vs 79.5 1/mwhr) (22.2 vs 21 gal/mwhr), and the flow rate from the steam/hot water scrubbers cannot be compared with anything, the values for flow from the high energy scrubber are about one-third of that predicted. However, the flow from the high energy scrubber does not take into account recirculation of the scrubber water which is done at the scrubber prior to clarification and which may account for the difference.

WASTE CHARACTERIZATION-COVERED ELECTRIC FURNACES WITH WET AIR POLLUTION CONTROL DEVICES

The data from Plant B provides information on the waste water from disintegrator scrubbers operating on covered furnaces producing silicon alloys. Raw waste loads of suspended solids and cyanides are given in Table 24 on the basis of the furnace power during the 16-hour sampling periods.

Table 24.	RAW WASTE	LCADS FOR	COVERED	FURNACES
	WITH DISI	NTEGRATOR S	SCRUBBERS	5

	Suspende	ed Solids	Cyaı	nides		Flow
<u>Product</u>		<u>lbs/mwhr</u>		lbs/mwhr	1/mwhr	<u>qal/mwhr</u>
SiMnZr	20.1	44.3	.0338	.0745	8270 8967	2185 2369
75% FeSi 50% FeSi	39.2 5.1	86.3 11.3	.0001	.0002	8823	2331
75% FeSi	6.8	15.0	.0139	.0307	7562	1998

The data for the second furnace in Table 24 probably represent reliable data, since at 75% particulate removal efficiency the suspended solids load is somewhat higher than are given in the EPA air pollution study (Ref. 32) data. The remaining data in Table 24 indicate suspended solids loads much lower than would be expected from the air emissions data. This could have either occurred due to poor functioning of the scrubbers (as evidenced by the lower temperature of the effluent water and observations of visible stack emissions, sometimes very heavy). Another possible explanation is that the samples may have been taken in a region where water sprays are used to suppress foaming, and could, therefore, have been diluted.

The data from Plant C provides raw waste load data for a sealed silicomanganese furnace where the off-gases are scrubbed in a spray tower and a disintegrator scrubber. These data are shown in Table 25.

Table 25.	RAW WASTE LOADS-SEALED SILICOMANGANESE
	FURNACE WITH DISINTEGRATOR SCRUEBER

Constituent	<u>kg/mwhr</u>	<u>lb/mwhr</u>
Suspended solids Phenol	16.6 .009	36.6 .019
Cyanide, total Cyanide, free	.044 .011	.098 .024
Chromium, total Manganese	.0004 4.858	0.001 10.70
	<u>l/mwhr</u>	<u>qals/mwhr</u>
Flcw	10,863	2,870

The data from Plant E also provide data on scrubber raw waste water loads from covered furnaces equipped with high energy and disintegrator scrubbers.

Table 26. RAW WASTE LCAD-COVERED FURNACES WITH SCRUEPERS

Constituent	<u>kq/mwhr</u>	<u>lbs/mwhr</u>
Susp. Solids	4.01	8.83
Phenol	0.002	0.004
Cyanide (Total)	0.007	0.015
Manganese	0.016	0.034
Chromium (Total)	0.002	0.004
	<u>l/mwhr</u>	<u>qals/mwhr</u>
Flow	9,746	2,575

The data from Plant H provide data on the raw waste loads from aluminothermic production of chromium alloys in which the off-gases are treated in a combination wet scrubber and baghouse and are given in Table 27.

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Constituent	<u>ka⁄kka</u>	<u>lb/ton</u>
Suspended Solids	3.6	7.1
Phenol	0	0
Cyanide (Total)	0	0
Cyanide (Free)	0	0
Manganese	0.0005	0.001
Chronium (Total)	2.98	5.95
Chromium (Hex.)	0.95	1.90
	<u>l/kkg</u>	<u>gals/tcn</u>
Flow	26,332	6,310

Table 27. RAW WASTE LCADS-ALUMINOTHERMIC SMELTING WITH COMBINATION WET SCRUBBERS AND BAGHOUSE

Since open furnaces produce greater volumes of gas than do covered furnaces, and since water usage in wet scrubbers is generally a function of gas volume treated, it was expected that open furnace scrubbers would have higher water usages than covered furnace scrubbers. Contrary to expectations, the covered furnaces which were surveyed had water uses higher than those of open furnaces using high energy scrubbers. This may be because water use in disintegrator scrubbers is higher, for a particular gas volume, than the water use in high energy scrubbers. Most of the covered furnaces surveyed used disintegrator, rather than high energy scrubbers. However, one furnace at Plant E was equipped with a high energy scrubber, and the water use on that equalled 9572 1/mwhr (2529 gal/mwhr), so it would seem that this explanation may not always be valid.

WASTE CHARACTERIZATION - SLAG PROCESSING

The data from Plant E provides information on the raw waste loads from slag processing operations. That from slag concentrating is shown in Table 28.

Constituent	<u>kg/kkg</u>	<u>lt/ton</u>
Suspended Solids Manganese Chromium, (Total)	46.0 .245 .109	91.9 .489 .217
	<u>1/kkq</u>	<u>qals/ton</u>
Flow	48,259	12,750

Table 28. RAW WASTE LOADS-SLAG CONCENTRATION PROCESS

No raw waste load can be calculated directly for the slag shotting process, since tonnage figures were not given. However, an estimate for tonnage can be made from production figures. The charge to alloy ratio is 3:1 for HC FeMn, meaning that three tons of charge materials are required to produce one ton of alloy. Assuming no losses, this means that two tons of slag and particulates are produced for every ton of alloy. The emission factor for HC FeMn is 335 lb/ton product, so the slag produced is two tons minus 335 lbs = 3665 lb/ton alloy. This figure times operating load divided by the electrical energy required per ton of alloy gives us an hourly production figure for slag of 24,452 lb/hr. This divided into the water flow rate gives a water use of 8,588 gal/ton processed, a suspended solids raw waste load of 15.5 lb/ton, and a manganese load of 3.87 lb/ton.

SECTION VI

SELECTION OF POLLUTANT PARAMETERS

Pollutant parameters have been selected by industry categories on the basis of those which originate in the production processes in significant amounts and for which control and treatment technologies are reasonably available. The parameters for each category have also been selected so as to be the minimum number which will insure control. The pollutant parameters selected are shown by category in Table 29.

Table 29. POLLUTANT PARAMETERS FOR INDUSTRY CATEGORIES

Parameters	Indust	ry Cat	eqory	
	<u>_ī</u> _	<u>_II</u> _	<u> </u>	
Suspended Solids	х	х	x	
pH	х	Х	X	
Total Chromium	х	Х	Х	
Hexavalent Chromium	х	X	-	
Total Cyanide	-	Х	-	
Manganese	х	Х	Х	
Phenol	-	Х	-	

Although effluent flow volumes are not specified in the recommended guidelines, its measurement and control is implicit in attaining the pollutant effluent loads specified. Flow, of course, is a basic parameter in that its magnitude indicates the degree of recirculation and reuse practiced and the degree to which water conservation is utilized. Additionally, flow measurements will be necessary for calculating treated waste loads for monitoring purposes.

Oil is not here considered as a parameter because it was found in lower concentrations in the raw waste than were allowable by the proposed guidelines. Additionally, oil is not associated with the process itself, but only appears as leaks from machinery, etc. At the levels detectable by the NPDES test methods, oil would be visible as a light sheen, and the plant would realize that there was an oil leakage somewhere.

Suspended solids are primary pollutants resulting from wet air pollution control devices and slag processing. Suspended solids concentrations may range up to 7600 mg/l. The pH determination in conjunction with metals determinations indicates that excessive free acidity or

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alkalinity has been neutralized after chromate reduction and precipitation, or cyanide destruction.

Chromium, manganese, iron, zinc, and aluminum are the principal metals originating in the production processes. Manganese concentrations may be as high as 1576 mg/l, while the maximum chromium concentrations found were 8.36 mg/l from an electrostatic precipitator spray tower and 121 mg/l from an exothermic chromium smelting operation. Hexavalent chromium is additionally included because it may be harmful at low levels.

Cyanide is not oxidized in the reducing atmospheres of covered furnaces and appears in the waste water. It must be considered in view of the potential danger as with hexavalent chromium.

Phenols evidently originate from electrode binding materials and are considered because of the taste-and-odor producing potential of even low concentrations of such compounds. They principally appear in the waste water from covered furnaces, although very small quantities may be present in that from open furnaces. It would seem that phenols are oxidized in open furnaces, but not in the reducing atmosphere of covered furnaces. Because they are evidently oxidized in open furnaces, phenols are not considered as a pollutant parameter for Category I.

Phosphate was originally considered as a pollutant parameter because it was present in some quantity in the wastewaters at a few plants. Examination of the data base for this pollutant, however, convinces us that it is generally present in fairly low concentrations in the raw waste, and drops out during treatment (even the rudimentary treatment given at some plants) to levels allowable by the proposed guidelines. Therefore, phosphate was dropped as a parameter after consideration of the costs of monitoring for a pollutant which will probably never exceed the guidelines.

The pollutant parameters chosen have been those which appeared in significant concentrations from the sampling and analysis conducted during the plant surveys, and are those parameters amenable to control. Other parameters such as dissolved solids, chlorides and sulfates appear effluents, but largely result from neutralization, softener in regeneration, and water reuse; they are thus a result of treatment and there would be no logic in attempting to set limits. Many of the metals contained in the raw waste, particularly iron, zinc, aluminum, and lead are part of the solids generated in the smelting furnaces. Plant survey indicates that they are controlled if suspended solids data concentrations are controlled.

Environmental Impact of Pollutant Parameters

The following is a discussion of the environmental impacts of the pollutant parameters selected for regulation:

Suspended Solids

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.

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 Suspended solids in water may interfere normal treatment processes. with many industrial processes, and cause foaming in boilers, or equipment exposed to water, especially as the Suspended solids are undesirable in water for encrustations on temperature rises. paper textile industries: and pulp; beverages; dairy products; laundries; dyeing; photography; cooling systems, and power plants. Suspended particles also serve as a transport mechanism for pesticides substances which are readily sorbed into or onto clay and other 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.

Turbidity is principally a measure of the light absorbing properties of suspended solids. It is frequently used as a substitute method of quickly estimating the total suspended solids when the concentration is relatively low.

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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. The relationship

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between pH and acidity or alkalinity is not necessarily linear or direct.

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, anđ foul stenches are aesthetic liabilities of any waterway. Even moderate changes from "acceptable" criteria limits of pH are deleterious to some The relative toxicity to aquatic life of many materials is species. increased by changes in the water pH. Metallocyanide complexes can increase a thousand-fold in toxicity with a drop of 1.5 pH units. The availability of many nutrient substances varies with the alkalinity and acidity.

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.

<u>Phenols</u>

Many phenolic compounds are more toxic than pure phenol; their toxicity varies with the combinations and general nature of total wastes. The effect of combinations of different phenolic compounds is cumulative.

Phenols and phenolic compounds are both acutely and chronically toxic to fish and other aquatic animals. Also, chlorophenols produce an unpleasant taste in fish flesh that destroys their recreational and commercial value.

It is necessary to limit phenolic compounds in raw water used for drinking water supplies, as conventional treatment methods used by water supply facilities do not remove phenols. The ingestion of concentrated solutions of phenols will result in severe pain, renal irritation, shock and possibly death.

Phenols also reduce the utility of water for certain industrial uses, notably food and beverage processing, where it creates unpleasant tastes and odors in the product.

<u>Cyanide</u>

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.

<u>Chromium</u>

Chromium, in its various valence states, is hazardous to man. It can produce lung tumors when inhaled and induces skin sensitizations. Large doses of chromates have corrosive effects on the intestinal tract and can cause inflammaticn of the kidneys. Levels of chromate ions that have no effect on man appear to be so low as to prohibit determination to date.

The toxicity of chromium salts toward aquatic life varies widely with the species, temperature, pH, valence of the chromium, and synergistic or antagonistic effects, especially that of hardness. Fish are relatively tolerant of chromium salts, but fish food organisms and other lower forms of aquatic life are extremely sensitive. Chromium also inhibits the growth of algae.

In some agricultural crops, chromium can cause reduced growth or death of the crop. Adverse effects of low concentrations of chromium on corn, tobacco and sugar beets have been documented.

Manganese

The presence of manganese may interfere with water usage, since manganese stains materials, especially when the pH is raised as in laundering, scouring, or other washing operations. These stains, if not masked by iron, may be dirty brown, gray or black in color and usually occur in spots and streaks. Waters containing manganous bicarbonate cannot be used in the textile industries, in dyeing, tanning, laundering, or in hosts of other industrial uses. In the pulp and paper industry, waters containing above 0.05 ppm manganese cannot be tolerated except for low-grade products. Very small amounts of manganese--0.2 to 0.3 ppm--may form heavy encrustations in piping, while even smaller amounts may form noticeable black deposits.

SECTION VII

CONTROL AND TREATMENT TECHNOLOGY

The water pollution control and treatment technology used in the ferroalloy industry has generally been sedimentation in lagoons, some of which are very large. The 8 plants which were surveyed in the course of the present study cover the full range of processes used in the industry and the various levels of control and treatment technology.

By far the most serious pollution problem to the industry has been that of air pollution. Air pollution abatement has been a major concern of the industry and has involved most of the expenditures for pollution control. Air pollution control systems installed, being built, or planned are generally capable of meeting existing state regulations; in cases where controls have been installed for 5 years or more, such controls were adequate to meet then-existing regulations, but may be marginal insofar as newer regulations are concerned.

The plants surveyed are classified in Table 30 in terms of the industry categorization given previously.

	Table 3	0. CHA	RACTERISTICS	OF	SURVEYED	PLANTS
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		بالا المالية المركز ا
<u>Plant</u>	Category	Processes and Water Uses and Air Controls
А		Baghouses being built, recirculated cooling water
В	II	Disintegrator scrubbers, once-through cooling water use
С	II	Sealed furnace, disintegrator scrubbers, recirculated cooling water and scrubber water
D	I	Steam/hot water scrubbers, recirculation of cooling and scrubber water
Ε	I,II,III	Disintegrator scrubbers, venturi scrubbers, once-through water use, slag processing
F		Baghouse/no air controls, recirculated cooling water
G	I,III	Electrostatic precipitators with water sprays, recirculated cooling water, slag processing
Н	II	Exothermic process, wet scrubbers and baghouse

The treatment and control technologies available for this industry's waste water may be grouped as follows for the principal waste parameters:

Suspended Solids: Water recirculation, lagoons, clarifier-flocculators, sand filters

pH: Neutralization

Chromium: Hexavalent chromium reduction, precipitation, sedimentation

Cyanide: Alkaline chlorination, ozonation

Manganese: Neutralization of acid salts, precipitation, sedimentation

Phenol: Biological oxidation, breakpoint chlorination, activated carbon

Water recirculation can be used to initially reduce the volume of water to be treated for suspended solids removal. Lagoons and clarifierflocculators can achieve effluent concentrations of 25 mg/l, when well operated. Lagoons are less expensive in capital and operating costs, but require much more land area. Sand filters achieve effluent concentrations of 10-15 mg/l and are little more expensive than clarifier-flocculators.

Neutralization is, of course, simply a matter of adding an acid or a base to achieve a neutral pH. This is most efficiently done with chemical feed pumps controlled by a pH instrument. A caustic or sulfuric acid solution can be used and pH controlled to within ± 0.2 of the desired pH.

Hexavalent chromium is reduced almost instantaneously at pH levels below 2.5 by sulfur dioxide. The pH is then raised with lime to about pH 8.2 and the reduced chromium is settled out. With proper operation, the hexavalent chromium should be completely reduced. The effluent concentration of total chromium depends upon good pH control and adequate sedimentation. Cyanide is oxidized rapidly to the less harmful form of cyanate at a pH of 10.5 by alkaline chlorination. Cyanate is oxidized to CO2 and N2 by continued chlorination at a pH of about 7.0 and a reaction time of about 60 minutes. Ozonation is an alternate method for the destruction of cyanide.

Manganese and iron, to the extent they are present as dissolved salts, are removed by neutralization of the acid salts, at a pH above 9.5 for manganese and above about 8 for iron. This is followed by precipitation and sedimentation. Ferrous hydroxide, in particular, forms a gelatinous precipitate which settles slowly. Sufficiently high pH, adequate sedimentation, and oxidation is required for low effluent concentrations.

Phenol can be oxidized biologically or chemically by chlorine and chlorine dioxide (Ref. 34). Chlorine dioxide must, of course, be generated on-site. Phenol can also be removed by absorption on

activated carbon. Biological oxidation may be unfeasible for this industry with its generally low BOD levels, although it may be usable if nutrients are added. Activated carbon absorption is also possible as a treatment technique, as is breakpoint chlorination.

The treatment processes discussed here are conventional. There does not appear to be any particular need for more advanced treatment methods. The main problems are the reduction of waste water volumes requiring treatment to the minimum, design of adequately sized facilities (particularly for suspended solids removal), proper operation (preferably with instrumental control), and operator training.

The choice of air pollution control technology is of importance in affecting waste water volumes. Most open furnaces are utilizing dry baghouses and, of course, produce no waste water effluent from this source.

There are only two known examples in the world of dry dust collectors being used on sealed or covered furnaces, neither of which is in the United States. The vast majority of covered furnaces use wet scrubbers; few open furnaces use wet systems. Some operations (such as exothermic) may require the use of such novel air systems as a wet baghouse.

Where a dash is shown under net concentration in Tables 31-89, except for those tables for intake water, no analysis was made for that parameter. Where a zero is shown under net concentration, but the maximum, minimum and average concentrations are represented by dashes, the parameter concentrations found were below the detectable limit for that parameter. In other cases where the net concentration is zero, it is because the average concentration is the same as or less than that of the intake water.

The test methods used for the constituents of the waters are as follows: pH - Standard Method No. 221, Aluminum, Chromium, Iron (Total), Lead, Manganese, and Zinc - Standard Method No. 129 (Atomic Absorption), Cyanide - Standard Method Nos. 207A, 207C, Phenol - Standard Method Nos. 222A, 222B and 222D, Phosphate - Standard Method No. 223E, and Suspended Solids - Standard Method No. 148C. With the exception of the test procedure for suspended solids, the tests used are identical with those specified for use for monitoring under the NPDES system (38 C.F.R., Part The test for suspended solids gives results 136). within the experimental error of the NPDES test method. 'Standard Method' refers to methods contained in "Standard Methods for Examination of Water and Wastewater," Thirteenth Edition, 1971, American Public Health Association.

PLANT A

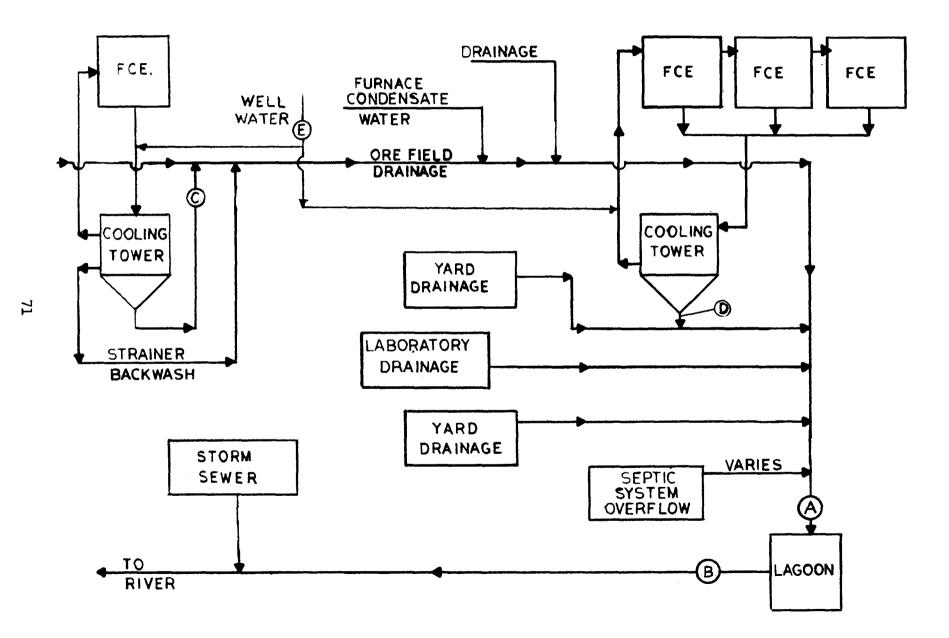
This plant was built in 1952 with five 10 mw submerged-arc open furnaces; at the time of our visit, three of these furnaces were still operating. A 35 mw furnace was built in 1968, and a 20 mw furnace is currently under construction. The large furnace produces 50-85 percent FeSi. The other furnaces produce 50 percent FeSi, proprietary silicon base alloys, and a rare earth silicide. Chromium alloys have been produced in the past. No wet air pollution controls are used; baghouses are being installed. The water use system is as shown in Figure 7.

All plant water is supplied from wells and the furnace cooling water is recirculated. The No. 1 cooling tower was built in 1952 and serves the three 10 mw furnaces. It is being automated and modified to include softeners and strainers, similar to the No. 2 cooling tower. The No. 2 cooling tower was built in 1968 to serve the 35 mw furnace. Proprietary treatment chemicals and sulfuric acid are used in each system. Blowdown from the Nc. 1 tower is manual and from No. 2 tower is automatically A softener is used in the No. 2 controlled by total solids levels. tower system with bulk salt used as a regenerant. Recirculated flow in the No. 1 tower system is 227 1/sec (3600 gpm) and can be increased to 341 1/sec (5400 gpm) if required by cooling needs. Recirculation flow the No. 2 tower system is 284 1/sec (4500 gpm). The total furnace in power during the sampling period was 48.1 mw. The cooling water use was thus 38.2 liters (10.1 gals.) per kwhr. Other furnaces exist in the plant, but have not been recently operated, and there are no plans to reactivate them. The treatment facilities consist only of a settling lagoon insofar as removal of constituents from the cooling tower blowdown and miscellaneous yard drainage is concerned.

A storm sewer had been installed to by-pass storm run off originating in the hills behind the plant. This has reduced the wet weather flow through the treatment lagoon.

Summarized data from the plant survey are shown for various sampling points as designated in Figure 7 in Tables 31 through 35. The temperature drop across cooling tower No. 1 was determined to be $6.7^{\circ}C$ (12°F). The operating power on the furnaces served by this tower during the sampling period was 21.9 mw.

Figure 7. PLANT A WATER AND WASTEWATER SYSTEMS



Constituent	Concentr Minimum	ations, m Maximum	g/l (exce Average	Net Average
	<u> </u>			
Suspended Solids	50	440	183	170
Total Chromium	0.01	0.01	0.01	0.01
Hexavalent Chromium	_	-	-	-
Total Cyanide	-		-	0
Free Cyanide	-		_	Ō
Manganese	1.08	1.08	1.08	0.76
Oil	1.8	6.4	4.3	3.5
Iron	0.99	1.78	1.39	1.36
Zinc	0.07	0.07	0.07	0.03
Aluminum	0.33	0.33	0.33	0.33
Phenol	0.07	1.00		0.06
Phosphate	1.29			
Lead	1.29	3.09	2.42	2.34
	-		-	0
pH (units)	5.4	7.6	6.7	-
Average Flow	= 6.7 l/s	ec. (106	ġpm)	

Table 32ANALYTICAL DATA -SPE - PLANT A
LAGOON EFFLUENT

			g/l (exce	pt as noted)
Constituents	Minimum	Maximum	Average	Net Average
Suspended Solids Total Chromium Hexavalent Chromium	20	440 0.01	73 -	60 0 0
Total Cyanide	_	-	_	0
Free Cyanide	-	-	-	0
Manganese	0.91	1.15	1.07	0.75
0i1	1.4	58.6	25.9	25.1
Iron	1.71	2.06	1.85	1.82
Zinc	0.05	0.06	0.05	0.01
Aluminum	-	-	-	0
Phenol	0.34	0.71	0.49	0.15
Phosphate	1.01	1.35	1.12	1.04
Lead			-	0
pH (units)	5.7	7.6	7.0	
Average Flow = Average Temper				

Constituent	Minimum	Maximum	Average	Net Average
Suspended Solids	34	38	36	23
Total Chromium		-	-	0
Hexavalent Chromium	-	-	-	0
Total Cyanide	-	-	-	0
Free Cyanide	-	~	-	0
Manganese	0.32	0.32	0.32	0
Oil	0.4	1.0	0.7	0
Iron	0.23	0.36	0.30	0.27
Zinc	0.03	0.08	0.05	0.01
Aluminum	-	-		0
Phenol	0.04	0.57	0.22	0
Phosphate	5.26	5.79	5.47	5.39
Lead	-	-	-	0
pH (units)	6.9	7.8	7.3	

Table 34 ANALYTICAL DATA -SPD - PLANT A COOLING TOWER #1

	Concentr	ations, m	g/l (exce	pt as noted)
<u>Constituents</u>	Minimum	Maximum	Average	Net Average
Suspended Solids Total Chromium Hexavalent Chromium Total Cyanide Free Cyanide Manganese Oil Iron Zinc Aluminum Phenol Phosphate	1.4 0.53 0.4 0.34 0.03 0.07 4.47	500 - - 0.53 0.8 0.38 0.055	183 - - 0.53 0.6 0.36	170 0 0 0.21 0 0.33 0 0 4.75
Lead pH (units)	6.6	8.3	7.4	0
Average Flow Average Tempe	= 1.55 1/s	ec. (24.	6 gpm)	

Constituent	Minimum	Maximum	Average	Net Average
Suspended Solids	8	16	13	_
Total Chromium	-	-	-	-
Hexavalent Chromium	-	-	-	-
Total Cyanide	-	-	-	-
Free Cyanide	-	-	-	-
Manganese	0.32	0.32	0.32	-
0il	0.6	1.0	0.8	-
Iron	-	0.06	0.03	-
Zinc	0.022	0.07	0.044	-
Aluminum	-	-	-	-
Phenol	0.30	0.41	0.34	-
Phosphate	-	0.14	0.08	-
Lead	-	-	-	-
pH (units)	6.9	7.7	7.3	-

Table 36 ANALYTICAL DATA -SPA - PLANT B INTAKE WATER

Constituents	Minimum	Maximum	Average	Net Average
Suspended Solids	4	38	20	-
Total Chromium	-	-	-	-
Hexavalent Chromium	-	-		-
Total Cyanide	-	0.016	0.005	-
Free Cyanide	-	-	-	-
Manganese	0.018	0.018	0.018	-
Oil	0.4	1.5	0.8	-
Iron	1.31	1.37	1.34	-
Zinc	0.02	0.02	0.02	-
Aluminum	-	-	-	-
Phenol	-	-		-
Phosphate	0.23	0.23	0.23	-
Lead	-	-	-	-
pH (units)	6.5	7.7	6.9	-

PLANT E

This plant has been operating since 1939 and has four covered submergedarc furnaces producing 50 percent ferrosilicon, 75 percent ferrosilicon and silicon-manganese-zirconium (SMZ). These furnaces have a total rating of 71.0 mw and operated during the plant survey period at 54.3 mw. The water and waste water system for the plant is shown in Figure 8.

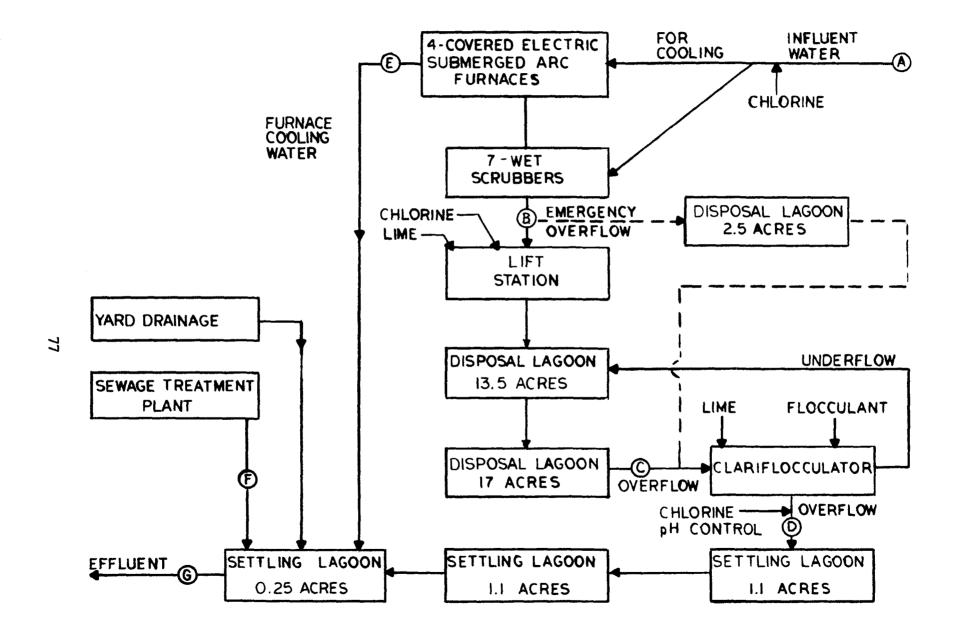
The four covered furnaces use cooling water on a once-through basis and the sewage by the 350 employees is treated at an on-site plant. The total effluent is 30,282 cu. m/day (8 mgd). Water is drawn from a surface source.

fumes from the four furnaces are scrubbed using seven Buffalo Forge The (disintegrator) scrubbers, each using 15.78 l/sec (250 gpm) of water. During the plant survey, one furnace had only one scrubber, each of the other furnaces had 2 scrubbers; a second scrubber was being installed on the first furnace. The scrubber water is combined at a lift station lime and chlorine are added to oxidize the cyanides produced in where the covered furnaces. The scrubber water then flows through 2 lagoons series totaling 30.5 acres in area and providing 5-6 days retention. in The flow then goes to a clariflocculator where lime and a flocculant are added for improved sedimentation. The clariflocculator underflow is returned to the first lagoon and the clariflocculator effluent is chlorine, lime being added if necessary, to destroy treated with The clariflocculator overflow effluent then passes residual cyanides. through 2 additional lagoons in series totaling 2.2 acres in area. The treated scrubber water is then combined with cooling water, sewage plant effluent, and yard drainage and flows through a final lagoon 0.25 acres in area. The cooling water temperature averages 8.33 °C (15°F) above (The plant states that the average temperature rise of the ambient. cooling water is 4-5.5°C (7-10°F)).

The total plant effluent was determined by measurements over а rectangular weir and the sewage plant effluent was measured by bucket and stopwatch. The yard drainage flow was estimated. The furnace cooling water flow was determined by difference and checked by a calculated chloride balance. The discharge permit data for this plant indicated a cooling water flow of 378.6 1/sec (6,000 gpm) and recirculation of some of this water. There is no chloride buildup and a low temperature increment in this system. The plant states that there is no evaporation associated with recirculation, which is done to increase water velocity in cooling passages. This recirculation may account for some of the difference between discharge permit data and that found during the plant survey. In light of the low temperature increment, however, it is doubtful that 43 percent of the cooling water is recirculated and the flow obtained during the plant survey was judged to be correct.

The total operating loads on the furnaces during the sampling was 54.3 mw. Summarized analytical data are shown for the sampling points as designated in Figure 8 in Tables 36 through 42.

Figure 8. PLANT B WATER AND WASTEWATER SYSTEMS



Constituent	Minimum	Maximum	Average	ot as noted) Net Average
Suspended Solids	968	2,242	1,555	1,535
Total Chromium		-	-	0
Hexavalent Chromium	-	_	-	0
Total Cyanide	1.18	3.28	2.49	2.48
Free Cyanide	0.20	1.57	1.04	1.03
Manganese	15.9	38.6	24.0	24.0
Oil	2.4	7.6	4.5	3.7
Iron	6.1	8.9	7.8	6.5
Zinc	1.46	3.10	2.10	2.08
Aluminum	0.69	1.29	0.99	0.99
Phenol	5.62	9.05	7.27	7.27
Phosphate	0.54	2.25	1.11	0.88
Lead	1.43	1.96	1.71	1.71
pH (units)	6.2	6.4	6.3	

Table 37 ANALYTICAL DATA -SPB · PLANT B WET SCRUBBERS

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Table	38	ANALYTICAL DATA -SPC - PLANT	B
		THICKENER INLET	

Constituents	Minimum	Maximum	Average	Net Average
Suspended Solids	70	96	83	63
Total Chromium	_	-	-	-
Hexavalent Chromium	-	-	-	0
Total Cyanide	0.15	0.36	0.22	0.21
Free Cyanide	0.15	0.36	0.22	0.21
Manganese	2.58	2.97	2.84	2.82
Oil	0.6	2.2	1.2	0.4
Iron	0.79	1.14	0.95	0
Zinc	0.94	1.08	1.01	0.99
Aluminum	-	0.29	0.19	0.19
Phenol	0.43	0.44	0.43	0.43
Phosphate	0.45	0.54	0.51	0.28
Lead	-	-	-	0
pH (units)	6.3	6.9	6.6	

	the second s			pt as noted)
Constituent	Minimum	Maximum	Average	Net Average
Suspended Solids	8	86	56	36
Total Chromium	_	0.01	-	0
Hexavalent Chromium	-	-	-	0
Total Cyanide	0.15	0.34	0.21	0.20
Free Cyanide	0.15	0.34	0.21	0.20
Manganese	0.88	0.93	0.90	0.88
Oil	1.2	3.0	2.2	1.4
Iron	0.41	0.50	0.47	0
Zinc	0.38	0.39	0.38	0.36
Aluminum	-	-	-	0
Phenol	0.49	0.51	0.50	0.50
Phosphate	0.27	0.54	0.41	0.18
Lead	-	0.05	0.03	0.03
pH (units)	8.2	9.6	9.0	

Table 39ANALYTICAL DATA -SPD- PLANT BTHICKENER OVERFLOW

Table 40 ANALYTICAL DATA -SPE - PLANT B COOLING WATER

	Concentr	ations, m	g/l (exce	pt as noted)
<u>Constituents</u>	Minimum	Maximum		Net Average
Suspended Solids Total Chromium Hexavalent Chromium Total Cyanide Free Cyanide Manganese Oil Iron Zinc Aluminum Phenol Phosphate Lead	4 - 0.006 0.025 0.6 1.20 0.044 0.47 0.22	22 0.061 0.025 0.8 1.34 0.044 0.47 0.22	11 0.025 0.025 0.7 1.27	0 0 0 0.020 0
pH (units)	6.7	8.5	7.9	

Average Flow = 217 l/sec. (3,440 gpm)

Constituent	Minimum	Maximum	Average	Net Average
Suspended Solids	20	48	32	12
Total Chromium	0.01	0.01	0.01	0.01
Hexavalent Chromium	_	_	-	0
Total Cyanide	-		-	Ő
Free Cyanide	-	-	_	õ
Manganese	1.52	1.52	1.52	1.50
Oil	1.0	2.6	2.0	1.2
Iron	0.33	1.31	0.82	0
Zinc	0.11	0.11	0.11	0.09
Aluminum	0.33	0.33	0.33	0.33
Phenol	-	-	-	0
Phosphate	6.31	6.31	6.31	6.08
Lead	-	-	-	0
pH (units)	6.6	7.6	7.2	

Table 42ANALYTICAL DATA -SPG - PLANT BTOTAL PLANT DISCHARGE

Constituents	Minimum	Maximum	Average	Net Average
Suspended Solids	10	70	35	15
Total Chromium		0.02	C.01	0.01
Hexavalent Chromium		-	-	-
Total Cyanide	0.006	0.030	0.020	0.015
Free Cyanide	0.006	0.020	0.010	0.010
Manganese	0.20	0.22	0.21	0.19
Oil	1.0	2.6	1.6	0.8
Iron	0.24	0.28	0.27	0
Zinc	0.08	0.11	0.09	0.07
Aluminum	0.22	0.35		
Phenol	0.11		0.12	0.12
Phosphate	0.30			
Lead		-	-	0
pH (units)	8.1	9.2	8.5	

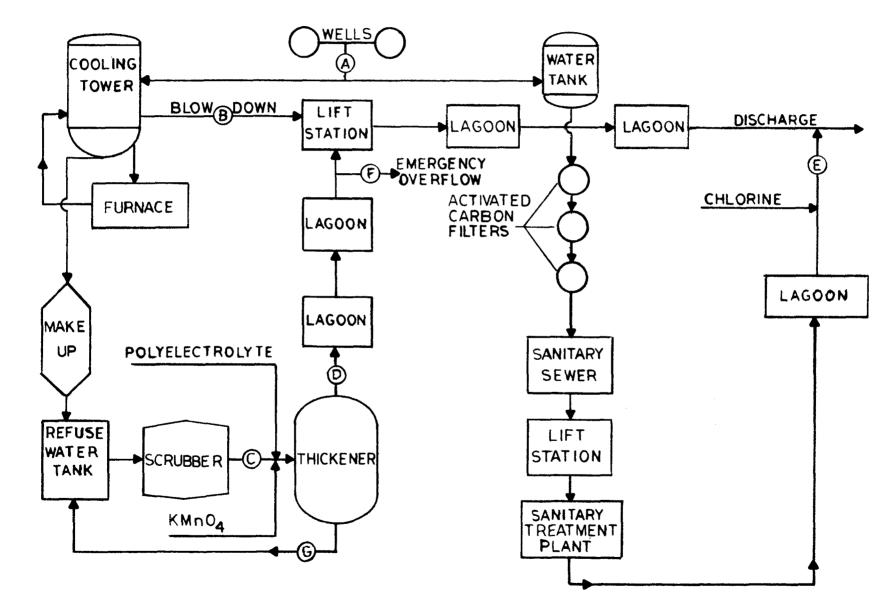
PLANT C

This plant was built in 1967 and has a single sealed furnace rated at 33 mw. The principal product is silicomanganese.

The water use and waste treatment system is shown in Figure 9. The furnace off-gases are scrubbed in a spray tower and a low energy (Dingler) scrubber. Water is recycled and reused in both the scrubber system and the furnace cooling water system; the latter incorporates a cooling tower. Makeup for the scrubber system is attained from blowdown from the cooling water system. The scrubber effluent is treated with potassium permanganate to oxidize the cyanides and a flocculant aid to improve sedimentation in the thickener to which all of the scrubber The thickener overflow is recycled to the scrubbers and water flows. the underflow is treated in a series of 2 lagoons. The effluent of these lagoons and the cooling tower blowdown are combined and flow through 2 additional lagoons in series. The sanitary sewage is treated in a package-type plant and allowed to settle in a small lagoon before being combined with the industrial waste water for discharge. The tower recirculation rate is 163 1/sec (2580 cooling qpm). The temperature drop across the cooling tower is 14°C (25.2°F).

Summarized analytical data are shown for the designated sampling points in Tables 43 through 49.

Figure 9. PLANT C WATER AND WASTEWATER SYSTEMS



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Constituent	Minimum	Maximum	Average	Net Average
Suspended Solids	-	2	1	-
Total Chromium	-	-	-	-
Hexavalent Chromium	-	-	-	-
Total Cyanide	-	-	-	_
Free Cyanide	-	-	-	-
Manganese	0.013	0.017	0.016	
Dil	_	0.4	0.2	-
Iron	0.51	0.51	0.51	-
Zinc	0.021	0.029	0.026	-
Aluminum	-	-	_	-
Phenol	-	_	-	-
Phosphate	-	-	-	-
Lead	-	-	-	-
pH (units)	6.9	7.5	7.2	

Table 44ANALYTICAL DATA -SPB - PLANT CCOOLING TOWER BLOWDOWN

Constituents	Minimum	Maximum	Average	Net Average
Suspended Solids	40	50	45	44
Total Chromium	_	_	-	0
Hexavalent Chromium	-	-	-	0
Total Cyanide	1.37	3.81	2.21	2.21
Free Cyanide	-	-	-	-
Manganese	49	56	52	52
Oil	0.6	1.2	0.9	0.7
Iron	0.51	0.68	0.57	0.06
Zinc	3.32	3.40	3.35	3.32
Aluminum	-	-	-	-
Phenol	0.14	0.24	0.19	0.19
Phosphate	0.28	0.95	0.50	0.50
Lead	-	-	-	-
pH (units)	7.6	7.8	7.7	
Average Flow Average Tempe	•			

Constituent	Minimum			pt as noted) Net Average
Suspended Solids	2	8	6	5
Total Chromium			_	0
Hexavalent Chromium	-	-	-	0
Total Cyanide	-			0
Free Cyanide	-			0
Manganese	3.5	6.3	5.0	5.0
Oil	1.0	1.6	1.3	1.1
Iron	0.42	0.47	0.44	0
Zinc	0.181	0.181	0.181	0.155
Aluminum	-		-	0
Phenol	0.04	0.29	0.17	0.17
Phosphate		-	-	
Lead	-	-	-	0
pH (units)	5.2	7.0	6.1	·

Table 49ANALYTICAL DATA -SPE- PLANT CSEWAGE PLANT EFFLUENT

Table 50 ANALYTICAL DATA -SP.F - PLANT C SLUDGE LAGOON EFFLUENT

Constituents	Minimum	Maximum	Average	Net Averag
Suspended Solids	106	312	188	187
Total Chromium		-	-	0
Hexavalent Chromium	-	-	-	0
Total Cyanide	1.85	2.41	2.15	2.15
Free Cyanide	0.32	1.08	0.77	0.77
Manganese	65	97	75.5	75.5
Dil	1.4	2.4	1.9	1.7
Iron	1.11	1.64	1.30	0.79
Zinc	1.93	3.11	2.51	2.48
Aluminum	9.4	11.1	10.0	10.0
Phenol	0.15	0.36	0.23	0.23
Phosphate	1.52	2.23	1.82	1.82
Lead	-	0.77	0.50	0.50
pH (units)	7.3	7.7	7.5	

Constituent Minimum Maximum		
	Average	Net Average
ended Solids 100 252 1 Chromium	181	180 0
valent Chromium	-	0
l Cyanide 5.01 6.48	5.60	5.60
Cyanide 0.73 1.12	0.90	0.90
anese 51 82	71	71
2.8 4.0	3.4	3.2
0.27 0.43	0.38	0
1.00 2.80	1.73	1.70
inum 4.1 9.4	6.2	6.2
ol 0.47 0.86	0.64	0.64
phate 1.02 4.0	2.05	
- 0.80		0.49
units) 7.2 7.7	7.5	
- -	0.80 7.7	0.80 0.49 7.7 7.5

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Table	52	ANALYTICAL	DATA	-SPA	-	PLANT	D
		WELL WA	ATER				

Constituents	Minimum	Maximum	and the second s	pt as noted) Net Average
Suspended Solids	10	16	13	-
Total Chromium		-	-	-
Hexavalent Chromium		-	-	-
Total Cyanide	-	-	-	-
Free Cyanide	-		-	-
Manganese	0.20	0.20	0.20	-
Oil		-	-	
Iron	2.24	2.30	2.27	-
Zinc	0.026	0.026	0.026	-
Aluminum	-	-	-	 .
Phenol	-	-		-
Phosphate	0.02	0.04	0.03	-
Lead	-	-	-	-
pH (units)	6.1	7.9	6.7	-

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	Concentrations, mg/l (except as noted				
Constituent	Minimum	Maximum	Average	Net Average	
Suspended Solids	100	252	181	180	
Total Chromium	-	-	-	0	
Hexavalent Chromium	-	-	-	0	
Total Cyanide	5.01	6.48	5.60	5.60	
Free Cyanide	0.73	1.12	0.90	0.90	
Manganese	51	82	71	71	
Oil	2.8	4.0	3.4	3.2	
Iron	0.27	0.43	θ.38	0	
Zinc	1.00	2.80	1.73	1.70	
Aluminum	4.1	9.4	6.2	6.2	
Phenol	0.47	0.86	0.64	0.64	
Phosphate	1.02	4.0	2.05	2.05	
Lead		0.80	0.49	0.49	
pH (units)	7.2	7.7	7.5		

Table 49ANALYTICAL DATA -SPG- PLANT CTHICKENER OVERFLOW

Average Flow = 67.71/sec.(1,075 gpm)

Table	50	ANALYTICAL DATA -SPA - PLANT	D
		WELL WATER	

Constituents	Minimum	Maximum	Average	Net Average
Suspended Solids	10	16	13	-
Total Chromium	-			-
Hexavalent Chromium	-	-		
Total Cyanide	-	-	-	-
Free Cyanide	-	-	-	-
Manganese	0.20	0.20	0.20	-
Oil	~		_	
Iron	2.24	2.30	2.27	
Zinc	0.026	0.026	0.026	-
Aluminum		-	-	
Phenol	-	-	-	-
Phosphate	0.02	0.04	0.03	-
Lead	-	-	-	-
pH (units)	6.1	7.9	6.7	-

PLANT D

This plant has open submerged-arc furnaces which produce ferrochromium, ferrosilicon, blocking chrome, and ferromanganese. Three of the furnaces are rated at 5.5 mw and the fourth at 16.5 mw.

These furnaces are equipped with a new type of dust-removal system utilizing waste heat from the furnace to provide the energy for gas scrubbing without the use of exhaust fans. This system has recently been installed on four ferroalloy furnaces. The reaction gas passes through a heat exchanger, a nozzle, and a separator. The heat from the reaction gases is transferred to the water in the heat exchanger, increasing the temperature of the water to about 177-204°C (350-400°F) and the water pressure to about 21 kg/sq cm (300 psi). As the heated is expanded through the nozzle of the scrubber, partial flashing water occurs, and the remaining liquid is atomized. Thus, a two-phase mixture of steam and small droplets leaves the nozzle at high velocity. The reaction gas from the furnace is entrained by this high velocity, twophase mixture, and in the subsequent mixing, the reaction gas is scrubbed and cleaned. At the same time, the action of the gases leaving the nozzle aspirates the reaction gases from the furnace and propels them through the system. The mixture of steam, gas, and water droplets entrained with the collected particulates from the gas passes through a separator after discharge from the mixing section. The water and dust are removed from the gas-steam mixture; the gas leaves the separator through the stack, and the water and dust are discharged from the separator to a waste water treatment system. Chemicals and other treatment are applied to settle the solids and other contaminants from the water, and the fluid slurry is discharged to settling ponds. This system is illustrated in Figure 10. The water is then filtered, softened, and returned to a pump for recycling to the heat exchanger. Makeup water is added to replace any losses.

The water flow diagram is shown in Figure 11. The clarifiers consist of 3 inclined, tube-type clarifier-flocculators in parallel. The filters are 3 deep-bed sand filters in parallel; backwash on the filters is controlled by a continuously reading turbidimeter. The softener is a fluidized moving-bed ion exchange unit, rated at 38 l/sec (600 gpm). The particular softener design is claimed to minimize resin attrition to less than 1 percent per year and to minimize rinsewater requirements.

The recirculation rate at the cooling tower is 284 l/sec (4500 gpm), and the blowdown rate is 1.3 percent, or 3.7 l/sec (58.5 gpm). The temperature change across the tower is 7.2°C (13°F).

During the sampling period, 2 of the smaller furnaces were operating as was the largest furnace. The products produced were blocking chromium, ferrochromium, and 50 percent ferrosilicon. The average daily power consumption on the furnaces totaled 695.5 mwhr. Summarized analytical data for various sampling points as designated in Figure 11 are shown in Tables 50 through 55.

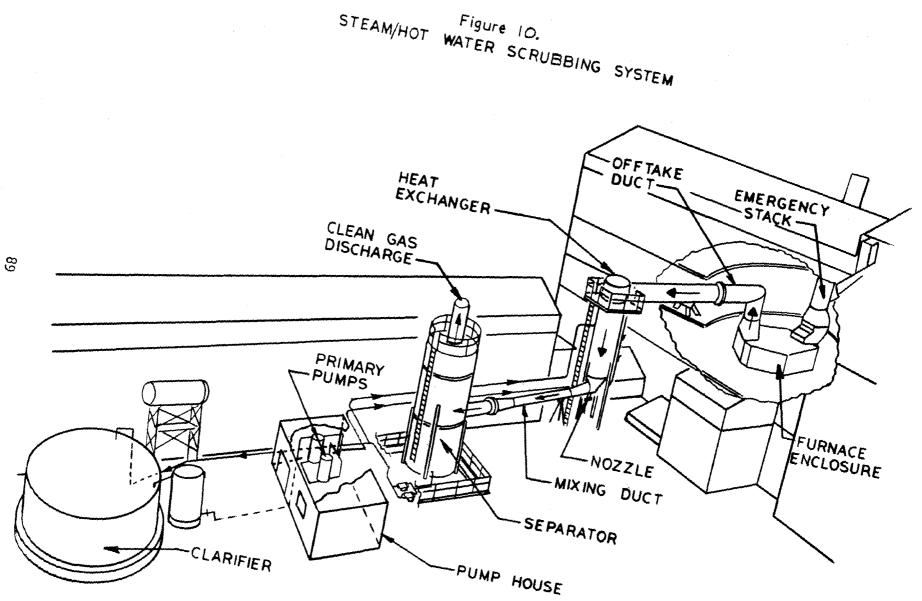
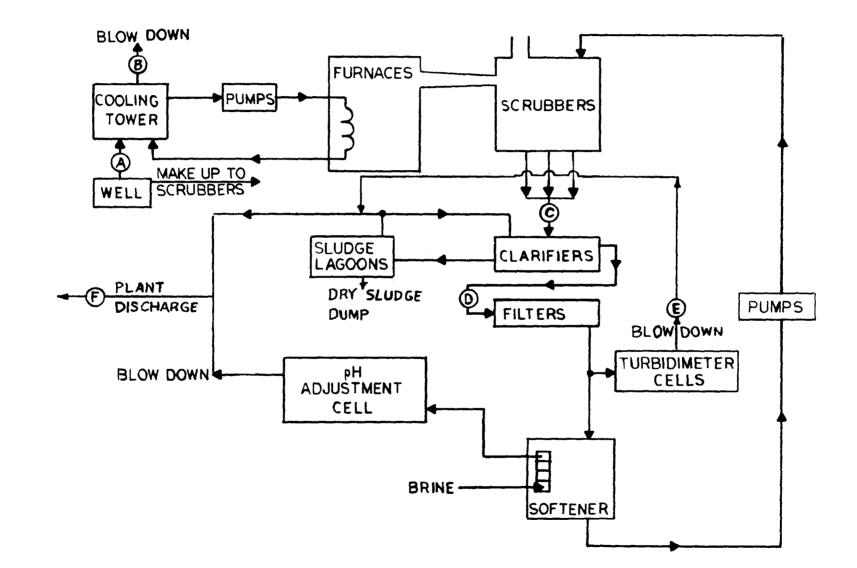


Figure 11. PLANT D WATER AND WASTEWATER SYSTEMS



06

	Concentr	ations, m	g/l (exce	pt as noted)
Constituent	Minimum	Maximum	Average	Net Average
Suspended Solids	10	28	19	6
Total Chromium	_		-	0
Hexavalent Chromium	-		-	0
Total Cyanide	0.007	0.007	0.007	0.007
Free Cyanide	-	-		-
Manganese	0.09	0.14	0.11	0
Oil	0.2	0.2	0.2	0.2
Iron	3.08	3.15	3.10	0.83
Zinc	0.059	0.077	0.069	0.043
Aluminum	0.7	0.7	0.7	0.7
Phenol	-	-	-	-
Phosphate	1.95	2.77	2.54	2.51
Lead	-	-	-	0
pH (units)	6.2	7.8	6.8	

Table 51ANALYTICAL DATA -SPB- PLANT DCOOLING TOWER BLOWDOWN

Table 52 ANALYTICAL DATA -SPC - PLANT D SLURRY BLEND TANK

	Concentr	ations, mo	g/l (excep	t as noted)
<u>Constituents</u>	Minimum	Maximum	Average	Net Average
Suspended Solids Total Chromium Hexavalent Chromium Total Cyanide Free Cyanide Manganese Oil Iron Zinc Aluminum Phenol Phosphate	Minimum 768 0.10 0.06 - 2.47 11.2 10.8 0.03 0.45	Maximum 7,644 3.37 1.85 0.062 4.06 1.3 60. 34. 103. 0.48 6.95	3,070 1.24 0.68 2 0.031 0 0.018	3,057 1.24 0.68 0.031 0.018 1.69
Lead pH (units)	0.68 8.7	4.4 9.3	3.03 9.0	3.03

Average Flow = 21.6 l/sec. (343.5 gpm)

Constituent	Minimum	Maximum	Average	Net Average
Suspended Solids	8	102	38	25
Total Chromium	-	2.24	0.46	0.46
Hexavalent Chromium	-			-
Total Cyanide	-	0.014	0.005	0.005
Free Cyanide	-	-	-	-
Manganese	0.05	0.60	0.25	0.05
Oil	0.2	1.6	1.0	1.0
Iron	0.39	0.77	0.57	0
Zinc	0.173	0.325	0.175	0.149
Aluminum	-	0.6	0.2	0.2
Phenol	0.02	0.30		0.12
Phosphate	0.04	0.10		0.03
Lead	-	-	_	0
pH (units)	7.1	11.1	9.6	-

Table 53 ANALYTICAL DATA -SPE- PLANT D CONTINUOUS BLOWDOWN

Table 54 ANALYTICAL DATA -SPD - PLANT D FILTER SUPPLY TANK

Constituents	Minimum	Maximum	Average	Net Average
Suspended Solids	68	134	112	99
Total Chromium	0.25	0.43	0.31	0.31
Hexavalent Chromium	-	-	-	-
Total Cyanide	0.020	0.029	0.024	0.024
Free Cyanide	-	-	-	-
Manganese	0.42	1.23	0.78	0.58
Oil	0.3	1.6	1.1	1.1
Iron	1.53	6.15	3.15	0.88
Zinc	0.288	2.51	1.24	1.21
Aluminum	0.7	1.8	1.3	1.3
Phenol	-	0.23	0.12	0.12
Phosphate	0.01	0.18	0.07	0.04
Lead	-	0.42	0.14	0.14
pH (units)	9.1	10.3	9.7	

Constituent	Minimum			ot as noted) Net Average
Suspended Solids	60	532	1 86	173
Total Chromium	0.54	1.35	0.87	0.87
Hexavalent Chromium	0.138	0.215		0.177
Total Cyanide	0.014	0.030	0.025	0.025
Free Cyanide		-		—
Manganese	0.81	3.25	1.81	1.61
Oil	0.4	0.61	0.54	0.54
Iron	1.06	7.83	3.79	1.52
Zinc	0.592	3.79	2.03	2.00
Aluminum	-		-	0
Phenol		0.05	0.02	0.02
Phosphate	-	0.10	0.06	0.03
Lead	-	0.63	0.21	0.21
pH (units)	8.4	9.6	8.9	

Table 55 ANALYTICAL DATA -SPF- PLANT D PLANT DISCHARGE

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FLANT E

This plant has been operating since 1951 and has principally two areas where waste waters other than cooling waters are generated and discharged. These two areas contain electric arc furnaces and electrolytic cells, respectively.

There are seven covered and two open submerged-arc furnaces where 50 percent ferrosilicon, silicomanganese, standard and medium carbon ferromanganese, and high carbon ferrochromium are produced. This area also contains metals refining and slag shotting operations. These furnaces have a total rating of 126 mw and operated during the survey period at 82 mw.

The nine furnaces use cooling water on a once-through basis. The sanitary sewage is treated at an on-site plant and discharges with the cooling water. The total plant effluent is 1.16 X 10⁶ cu. m/day (305.5 mgd), the majority of which is cooling water from the plant's power generating station.

The water and waste water systems for the plant are shown in Figure 12. Also shown in this figure are the sampling points used during the survey.

The fumes from the furnaces are scrubbed with either venturi or disintegrator type scrubbers. There are five venturi and 12 disintegrator type scrubbers available for the nine furnaces. The scrubbers use between 22-32 1/sec (350-500 gpm) of the water when operating. The metals refining operation also utilizes a venturi scrubber. The scrubber water flows via a common line to the first of two lagoons operated in series. The lagoons have a combined surface area of 78 acres. The wash water from the electrolytic operations mixes with the scrubber waste water before entering the lagoons.

The acid waste water from the electrolytic operations flows to the second of these lagoons where a hydrated lime slurry is also added as a neutralizing agent. This second lagoon also receives the effluent from a flyash removal system at the power plant. The effluent from the second lagoon flows to the receiving stream.

A waste water discharge from the slag concentrator flows to a separate 4.3 acre tailings lagoon and then to the receiving stream.

Summarized analytical data for sampling points as designated in Figure 12 are shown in Tables 56 through 72. The 1971 average temperature increase in cooling water temperatures over inlet was $3.9^{\circ}C$ (7°F).

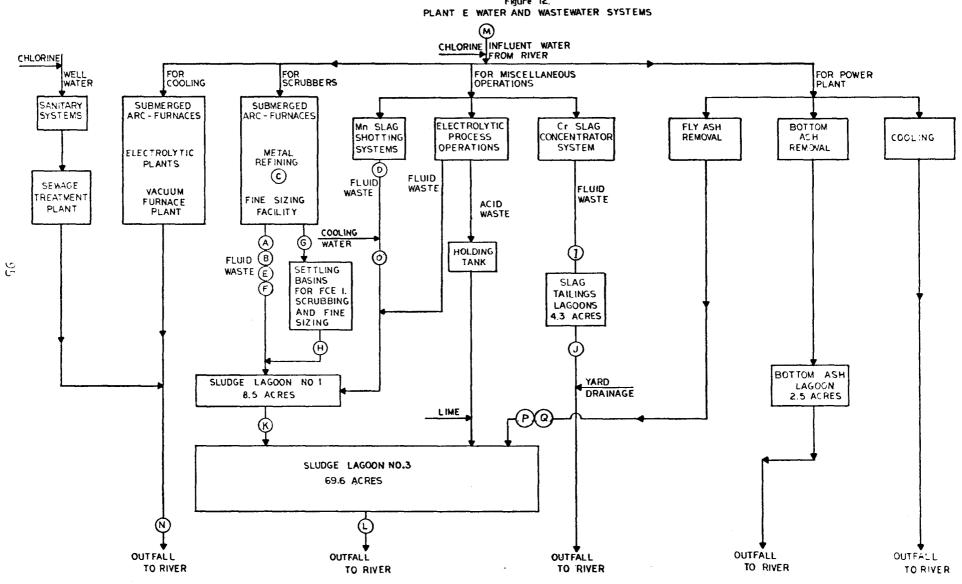


Figure 12.

Table 56 ANALYTICAL DATA -SPA- PLANT E FURNACE A SCRUBBER DISCHARGE

	Concentr	ations, m	g/l (exce	pt as noted)
Constituent	Minimum	Maximum	Average	
Suspended Solids Total Chromium Hexavalent Chromium Total Cyanide Free Cyanide Manganese Oil Iron Zinc Aluminum Phenol Phosphate Lead	210 0.01 - 54 1.2 5.26 18 4.45 - 1.79	342 0.01 - 54 1.2 5.26 18 4.45 - 1.79	261 0.01 - 54 1.2 5.26 18 4.45 - 1.79	228 0 0 54 1.2 4.68 18 3.78 0 0 1.79
рн (units)	7.0	7.1	7.0	

Average Flow = 28.4 l/sec. (450 gpm)

Table 57 ANALYTICAL DATA -SPB - PLANT E FURNACE B SCRUBBER DISCHARGE

				pt as noted)
Constituents	Minimum	Maximum	Average	Net Average
Suspended Solids Total Chromium	318 0.0 9	426 0.09	373 0.09	340 0.09
Hexavalent Chromium	-	-	_	-
Total Cyanide	0.87	0.87	0.87	0.87
Free Cyanide		-	-	~
Manganese	256	256	256	256
Oil	1.6	1.6	1.6	1.6
Iron	18.0	18.0	18.0	17.4
Zinc	48	48	48	48
Aluminum	13.0	13.0	13.0	12.3
Phenol	0.22	0.22	0.22	0.22
Phosphate	-	-	-	0
Lead	5.6	5.6	5.6	5.6
pH (units)	6.4	6.9	6.7	
Average Flow =				

Table58ANALYTICAL DATA -SPC-PLANT E

METALS REFINING S	RUBBER DISCHARGE
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Constituent	Minimum	Maximum	Average	Net Average
Suspended Solids	874	1,674	1,204	1,171
Total Chromium	0.06	0.06		0
Hexavalent Chromium	-		-	-
Total Cyanide	-	_	-	0
Free Cyanide	-	· ·	-	0
Manganese	597	597	597	597
Oil	1.2	1.2	1.2	1.2
Iron	1.82	1.82	1.82	1.24
Zinc	0.46	0.46	0.46	0.44
Aluminum	0.87	0.87	0.87	0.20
Phenol	-	-	-	0
Phosphate	-		-	0
Lead	-			0
pH (units)	7.8	8.7	8.2	

Table 59 ANALYTICAL DATA -SPD - PLANT E SLAG SHOTTING WASTEWATER

	Concentr	ations, m	g/l (exce	pt as noted)
Constituents	Minimum	Maximum	Average	Net Average
Suspended Solids Total Chromium Hexavalent Chromium Total Cyanide Free Cyanide Manganese Oil Iron Zinc Aluminum Phenol Phosphate Lead pH (units)	132 0.03 - 54 1.2 0.28 0.13 10.5 - 7.3	302 0.03 - - 54 1.2 0.28	217 0.03 - - 54 1.2 0.28 0.13	184 0 0 54 1.2 0 0.11 9.8 0 0
Average Flow = (about 20 mun/m		ec. (1,75	0 gpm)	

Table 60ANALYTICAL DATA -SPE- PLANT EFURNACE CSCRUBBER DISCHARGE

<u>Constituent</u>	Minimum	Maximum	Average	Net Average
Suspended Solids	264	364	317	284
Total Chromium	0.57	0.57	0.57	0.41
Hexavalent Chromium	-	_	-	
Total Cyanide	0.16	0.16	0.16	0.16
Free Cyanide	-	-		-
Manganese	21.9	21.9	21.9	21.4
Oil	1.8	1.8	1.8	1.8
Iron	3.19	3.19	3.19	2.61
Zinc	8.7	8.7	8.7	8.7
Aluminum	7.1	7.1	7.1	6.4
Phenol	0.09	0.09	0.09	0.09
Phosphate	0.32	0.32	0.32	0.32
Lead	0.26	0.26	0.26	0.26
pH (units)	7.3	7.3	7.3	

Table 61 ANALYTICAL DATA -SPF - PLANT E FURNACE D SCRUBBER DISCHARGE

	Concentr	ations, m	g/l (exce	pt as noted)
Constituents	Minimum	Maximum	Average	Net Average
Suspended Solids Total Chromium	268	414	343	310
Hexavalent Chromium	0.10	0.10	0.10	0
Total Cyanide Free Cyanide	0.96	0.96	0.96	0.96
Manganese	4.22	4.22	4.22	
Oil Iron	1.6 4.00	$1.6 \\ 4.00$	1.6 4.00	1.6 3.42
Zinc Aluminum	3.00			2.98
Phenol	1.68 0.15		1.68 0,15	1.01 0.15
Phosphate Lead	0.50 1.03	-	0.50 1.03	0.50 1.03
pH (units)	4.4	4.4	4.4	1.05
Average Flow =	50.4 1/s	ec. (800	gpm)	

	Concentra	ations, mo	g/l (exce	pt as noted)
Constituent	Minimum	Maximum	Average	Net Average
Suspended Solids Total Chromium	-	4,140	•	3,720
Hexavalent Chromium	0.50	0.50	0.50	0.34
Total Cyanide	-	_		0
Free Cyanide	-	-	-	0
Manganese	1,576	1,576	1,576	1,576
Oil	-	-	-	-
Iron	6.94	6.94	6.94	6.36
Zinc	51	51	51	51
Aluminum	178	178	178	177
Phenol	0.09	0.09	0.09	0.09
Phosphate	-	-	-	0
Lead	11.7	11.7	11.7	11.7
pH (units)	8.6	8.7	8.6	
Average Flow =	44.1 l/s	ec. (700	gpm)	

Table 63 ANALYTICAL DATA -SPH - PLANT E FURNACE E SCRUBBER SETTLING BASIN DISCHARGE

	Concentra	ations, mg	/l (exce	ot as noted)
Constituents	Minimum	Maximum	Average	Net Average
Suspended Solids	3,348	11,364	6,080	6,047
Total Chromium	0.17	0.17	0.17	0.01
Hexavalent Chromium	-			
Total Cyanide		-		0
Free Cyanide	-		-	0
Manganese	1,322	1,322	1,322	1,322
Oil	1.0		1.0	1.0
Iron	7.16	7,16	7.16	6.58
Zinc	89	89	89	89
Aluminum	178	178	178	177
Phenol	-	~-		0
Phosphate	-	-		0
Lead	9.1	9.1	9.1	9.1
pH (units)	8.5	8.6	8.6	
Average Flow =	44.1 1/s	ec. (700	gpm)	

Table64ANALYTICAL DATA -SPI - PLANT ESLAGCONCENTRATORWASTEWATER

Constituent	Minimum			ot as noted)
COnstituent	MINIMUM	Maximum	Average	Net Average
Suspended Solids	856	872	864	831
Total Chromium	2.04	2.04	2.04	1.88
Hexavalent Chromium	-	-	-	0
Total Cyanide	-	0.013	0.007	0.007
Free Cyanide	-		-	
Manganese	4.39	4.81	4.60	4.11
Oil	0.2	2.2	1.2	1.2
Iron	5.8	14.6	10.2	9.6
Zinc	0.22	0.22		0.20
Aluminum	10.7	10.7	10.7	10.0
Phenol	-	-	-	0
Phosphate	-	-	-	0
Lead	-	-	_	0
pH (units)	6.1	6.2	6.2	
		• .		

Average Flow = 107.11/sec. (1,700 gpm)

Table 65 ANALYTICAL DATA -SPJ - PLANT E SLAG TAILINGS POND DISCHARGE

Constituents	Minimum	Maximum	Average	Net Average
Suspended Solids	46	90	62	29
Total Chromium	0.02	0.16	0.09	0
Hexavalent Chromium	-	-	-	0
Total Cyanide	0.006	0.006	0.006	0.006
Free Cyanide		-	-	
Manganese	0.95	1.26	1.08	0.59
Oil	-	-	-	0
Iron	1.14	1.54	1.32	0.74
Zinc	0.032	0.058	0.048	0.026
Aluminum	0.72	1.13	0.86	0.19
Phenol	0.25	0.25	0.25	0.25
Phosphate	-	-	-	0
Lead		-	-	0
pH (units)	6.2	6.9	6.4	

Average Flow =107.1 1/sec. (1,700 gpm)

				ot as noted)
Constituent	Minimum	Maximum	Average	Net Average
Suspended Solids	32	972	183	150
Total Cnromium	0.55	1.2	0.77	0.61
Hexavalent Cnromium	0.190	0.205	0.198	0.198
Total Cyanide	-	-	÷	0
Free Cyanide	-	-	-	0
Manganese	24.4	26.1	25.4	24.9
Oil	0.4	0.4	0.4	0.4
Iron	0.86	1.49	1.28	0.70
Zinc	4.22	7.90	5.55	5.53
Aluminum	1.44	2.60	2.04	1.37
Phenol	~	-	-	0
Phosphate	~		-	0
Lead	-	0.06	0.04	0.04
pH (units)	6.7	7.0	6.8	

 Table
 66
 ANALYTICAL
 DATA
 -SP
 K
 PLANT
 E
 LAGOON #3 INFLUENT

Average Flow =447.3 l/sec. (7,100 gpm)

Table 67 ANALYTICAL DATA -SP L - PLANT E LAGOON #3 EFFLUENT

	Concentr	ations, m	g/l (exce	pt as noted)
Constituents	Minimum	Maximum	Average	Net Average
Suspended Solids	2	30	15	٥
Total Chromium	0.08	0.08	0.08	0
Hexavalent Chromium	_	-	_	
Total Cyanide	-	0.008	0.005	0.005
Free Cyanide	-		-	0
Manganese	86	93	91	91
Oil	-	0.4	0.2	0.2
Iron	0.27	0.43	0.35	0
Zinc	0.22	0.46	0.34	0
Aluminum	0.11	0.21	0.15	0
Phenol		-	-	0
Phosphate		2.73	0.9	0.9
Lead	-	-		0
pH (units)	7.0	7.2	7.2	
Average Flow =	632.81/s	ec. (10,0	45 gpm)	

Constituent	Minimum	Maximum	Average	pt as noted) Net Average
······································				
Suspended Solids	24	38	33	_
Total Chromium	0.16	0.16	0.16	-
Hexavalent Chromium		-	-	· -
Total Cyanide	-	-	-	-
Free Cyanide	-	-	-	_
Manganese	0.49	0.49	0.49	-
Oil	-	0.2	-	-
Iron	0.54	0.62	0.58	-
Zinc	0.022	0.022	0.022	-
Aluminum	0.67	0.67	0.67	-
Phenol	-	-	-	-
Phosphate	-	-	-	-
Lead	-	-	-	-
pH (units)	7.2	7.2	7.2	

Table 69 ANALYTICAL DATA -SPN - PLANT E COOLING WATER DISCHARGE

Constituents	Minimum	Maximum	Average	Net Average
Suspended Solids	90	176	125	92
Total Chromium	6.6	6.6	6.6	6.4
Hexavalent Chromium		-	-	0
Total Cyanide		0.014	0.005	0.005
Free Cyanide		-	-	-
Manganese	0.053	4.61	1.58	1.09
Oil	-	0.4	0.3	0.3
Iron	3.42	32.	15.0	14.4
Zinc	0.045	0.045	0.045	0.023
Aluminum	4.28	4.28	4.28	3.61
Phenol	-			0
Phosphate	1.98	1.98	1.98	1.98
Lead		-		0
pH (units)	3.8	7.2	5.4	

Suspended Solids Tota⊥ Chromium Hexavalent Chromium Total Cyanıde	148 0.02	192 0.02	170	1 7 7
Tota⊥ Chromium Hexavalent Chromium			2/0	137
Hexavalent Chromium		U. UZ	0.02	0.02
Total Cvanide		-	_	-
TO CAT CARITAC	-	-		0
Free Cyanide	_	_	_	Ō
Manganese	19.1	19.1	19.1	18.6
Oil	1.0	1.0	1.0	1.0
Iron	3.72	3.72	3.72	3.14
Zinc	0.049	0.049	0.049	0.027
Aluminum	4.95	4.95	4.95	4.28
Phenol	-	-		0
Phosphate	-	-	-	0
Lead	-	-	-	0
pH (units)	7.5	7.5	7.5	

Table 71 ANALYTICAL DATA -SP p - PLANT E FLY ASH INFLUENT TO LAGOON

	Concentrations, mg/l (except as note				
<u>Constituents</u>	Minimum	Maximum	Average	Net Average	
Suspended Solids	1,246	20,156	7,667	7,634	
Total Chromium	-	-		-	
Hexavalent Chromium	-	-	-	-	
Total Cyanide	-		-	-	
Free Cyanide	-	-	-	-	
Manganese		-		-	
Oiı			-	-	
Iron		-	- a.	-	
Zinc	-	-	-	-	
Aluminum		-	-	-	
Phenol	~	_	-	-	
Phosphate		•••	-	-	
Lead	-	-	-	-	
pH (units)	6.6	7.0	6.7		

Average Flow = 70.9 l/sec. (1,125 gpm)

				· · · · · · · · · · · · · · · · · · ·
				pt as noted)
Constituent	Minimum	Maximum	Average	Net Average
Suspended Solids Total Chromium	510	5,200	2,209	2,176
Hexavalent Chromium	-	-		-
Total Cyanide	-	-		-
Free Cyanide	-	-	_	
Manganese	-	-		-
Oil		-	_	-
Iron	-	-		-
Zinc	-	-	-	-
Aluminum	-	-	-	
Phenol	-			-
Phosphate		-	-	
Lead		-		
pH (units)	6.6	6.8	6.7	

Table 72 ANALYTICAL DATA $-SP_Q$ - PLANT E FLY ASH INFLUENT TO LAGOON

Average Flow =70.9 l/sec. (1,125 gpm)

Table 73 ANALYTICAL DATA -SPA - PLANT F INTAKE WATER

Constituents	Minimum	Maximum	Average	pt as noted) Net Average
Suspended Solids	17	17	17	-
Total Chromium	Ū.01	0.01	0.01	_
Hexavalent Chromium	-	_	_	_
Total Cyanide	_	-	-	_
Free Cyanide		-	-	-
Manganese	0.026	0.026	0.026	-
Oil	1.0	1.0	1.0	
Iron	-	-	-	-
Zinc	0.008	0.008	0.008	-
Aluminum	-	-		-
Phenol		-		-
Phosphate	-	-		-
Lead	-	-	-	
pH (units)	7.3	7.3	7.3	

PLANT F

This plant utilizes seven electric arc furnaces to produce a product line including 50 percent ferrosilicon, low carbon ferrochromesilicon, high carbon ferrochromium, low carbon ferrochromium and silicon metal. The furnaces range in size from 10 mw to 36 mw with a collective capacity of 142 mw. No wet air pollution devices are used; baghouses have been installed on some furnaces. The water use system is as shown in figure 13.

All plant water is supplied from wells and the furnace cooling water is recirculated. Blowdown from all three cooling towers is automatically controlled by total solids levels. Flow rate in the cooling tower serving 4 furnaces with a capacity of 51 mw is 76 1/sec (1200 gpm). Bleed-off from this unit is 5 1/sec (80 gpm) or 6.6 percent of the recirculating flow. Another cooling tower serving a 20 mw furnace has a flow rate of 50 1/sec (800 gpm) and a bleed-off of 1 1/sec (20 gpm) or 2.5 percent of the recirculating flow. Two additional furnaces with a capacity of 65 mw are served by a 316 1/sec (5000 gpm) recirculating flow and a bleed-off of 13 1/sec (200 gpm) or 4 percent of the flow. Water treatment in the cooling system consists of a chromate based proprietary compound and algaecides.

Except for the overflow from septic tanks and isolated roof drains, the cooling system bleed-off is the major source of the plant discharge. Yard drainage resulting from surface run-off is collected and transfered to a small off-site lagoon. Under normal conditions there is no discharge from the lagoon as accumulated waste water either evaporates or drains through the lagoon bottom.

With 6 furnaces operating during the sampling period at 92.8 mw, the cooling water use was thus 17.15 1/kwhr (4.53 gal/kwhr). A limited number of samples were collected at this plant and the analytical data are summarized in Tables 73 through 75. The temperature drop across the cooling tower is 5.6°C (10°F).

A slag concentration process is used at this plant which utilizes water on a completely closed recirculation system, the only discharge is blowdown to a closed lagoon i.e., a lagoon with no outlet. This process was not operating at the time of our visit. The plant reports the blowdown rate to be 1.58 l/sec (25 gpm) from this system, while the total circulation rate is 94.65 l/sec (1500 gpm).

Table 76ANALYTICAL DATA -SP B- PLANT FCOOLING TOWER BLOWDOWN

	Concentr	ations, m	g/l (exce	pt as noted)
<u>Constituent</u>	Minimum	Maximum	Average	Net Average
Suspended Solids Total Chromium Hexavalent Chromium Total Cyanide Free Cyanide Manganese Oil Iron Zinc Aluminum Phenol Phosphate Lead	14 10.8 0.015 - - 0.093 1.4 0.11 6.98 - -	14 10.8 0.015 	14 10.8 0.015 - - 0.093 1.4 0.11 6.98 - -	0 10.8 0 0.067 0.4
pH (units)	5.9	5.9	5.9	
Average Flow =	12.0 1/5	ec. (200	gpm)	

Table77ANALYTICAL DATA -SP.C - PLANT FPLANT DISCHARGE

	سنجال فالبسي وسيبوج بالتجار والكالا			pt as noted)
Constituents	Minimum	Maximum	Average	Net Average
Suspended Solids	14	14	14	0
Total Chromium	13.6	13.6	13.6	13.6
Hexavalent Chromium	0.008	0.008	0.008	-
Total Cyanide	0.010	0.010	0.010	0.010
Free Cyanide	-		-	-
Manganese	0.370	0.370	0.370	0.344
Oil	4.2	4.2	4.2	3.2
Iron	0.58	0.58	0.58	0.58
Zinc	6.98	6.98	6.98	6.97
Aluminum	0.67	0.67	0,67	0.67
Phenol	-	-		0
Phosphate	-	-		0
Lead	-	-	-	0
pH (units)	6.5	6.5	6.5	

PLANT G

This plant has two 35 mw open furnaces which produce ferrochromium and a slag concentration operation. At times ferrochromesilicon is produced here. The water flow diagram for the plant is shown in Figure 14. Air pollution control is by means of electrostatic precipitators which are preceded by spray towers. The gases from the furnaces are conditioned by the water sprays in the towers in order to improve the performance of the precipitators; ammonia is added to the spray water.

The water supply is purchased city water and originates from wells. The cooling water used on the furnaces is recirculated through a cooling tower at the rate of 316 l/sec (5000 gpm). The spray towers remove a portion of the particulates from the furnace gases prior to the precipitators; the resultant slurry passes through settling basins near the furnaces and then a lagoon which has been excavated from a slag pile.

The slag concentrator is a sink-float process in which slag fines are separated from larger, usable slag particles and in turn from recoverable metal. The products are thus slag for sale and metal for reuse; the waste is a slurry of slag fines. The waste stream is treated in 2 small lagoons in series prior to discharge to a stream.

Plant production has been reported at 245 kkgs (270 short tons) of alloy per day. Reference 32 indicates a factor of 4.2 mwhr per ton, i.e., a furnace load of 1,134 mwhr per day. Analytical data are summarized in Tables 78 through 83, for sampling locations designated in Figure 14.

PLANT G

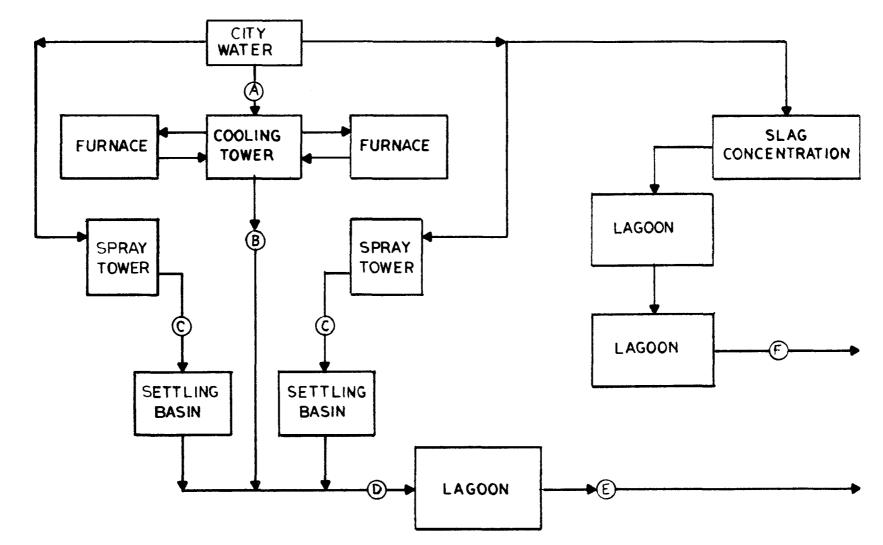
This plant has two 35 mw open furnaces which produce ferrochromium and a slag concentration operation. At times ferrochromesilicon is produced here. The water flow diagram for the plant is shown in Figure 14. Air pollution control is by means of electrostatic precipitators which are preceded by spray towers. The gases from the furnaces are conditioned by the water sprays in the towers in order to improve the performance of the precipitators; ammonia is added to the spray water.

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Plant production has been reported at 245 kkgs (270 short tons) of alloy per day. Reference 32 indicates a factor of 4.2 mwhr per ton, i.e., a furnace load of 1,134 mwhr per day. Analytical data are summarized in Tables 76 through 81, for sampling locations designated in Figure 14.

Figure 14. PLANT G WATER AND WASTEWATER SYSTEMS



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Constituent	Minimum	Maximum		pt as noted) Net Average
Suspended Solids	-	-	-	_
Total Chromium	_	_	_	
Hexavalent Chromium	-	-	-	_
Total Cyanide	-	-	_	-
Free Cyanide	-	-	-	_
Manganese	0.030	0.030	0.030	-
Oil	0.2	0.2	0.2	-
Iron	0.13	0.14	0.13	-
Zinc	0.159	0.159	0.159	-
Aluminum	-	-	-	-
Phenol	-	_	-	-
Phosphate	-	-	-	-
Lead	-	-	_	-
pH (units)	6.9	7.9	7.3	

Table 76 ANALYTICAL DATA -SP A PLANT G INTAKE CITY WATER

Average Flow = 20.5 l/sec. (325 gpm)

Table	77	ANALYT	ICAL 1	DATA	-SP	В –	PLANT	G
		COOLING	TOWER	BLOV	VDOW	N		

Constituents	Minimum	Maximum		pt as noted) Net Average
Suspended Solids	18	40	25	25
Total Chromium	3.23	3.35	3.31	3.31
Hexavalent Chromium	1.43	1.57	1.49	1.49
Total Cyanide	-	_	-	0
Free Cyanide	-	_	-	0
Manganese	0.094	0.094	0.094	0.064
oil	0.2	0.4	0.3	0.1
Iron	0.19	0.46	0.32	0.19
Zinc	0.52	0.71	0.65	0.491
Aluminum	0.98	0.98	0.98	0.98
Phenol	_	<u> </u>	-	0
Phosphate	0.05	0.15	0.12	0.12
Lead	-	_	_	0
pH (units)	7.3	8.4	8.0	

Constituent	Minimum	Maximum	Average	ot as noted) Net Average
Suspended Solids	A 13A	6,104	4 980	4 873
Total Chromium	2.66	•	4.76	-
Hexavalent Chromium	-	0.49		
Total Cyanide		-	-	0
Free Cyanide	* **	_	-	õ
Manganese	1.68	14.0	8.15	
Dil	0.2			
Iron		3.50		
Zinc		5.28		
Aluminum		23.0		
Phenol	_	÷		0
Phosphate	0.01	0.02	0.02	0.02
Lead	-	-		0
pH (units)	7.3	8.6	8.1	

Table 78 ANALYTICAL DATA -SP C PLANT G SPRAY TOWER DISCHARGE

Table 79 ANALYTICAL DATA -SP D PLANT G SETTLING BASIN EFFLUENT

	Concentr	ations, mo	g/l (exce	pt as noted)
<u>Constituents</u>	Minimum	Maximum	Average	Net Average
Suspended Solids Total Chromium Hexavalent Chromium Total Cyanide Free Cyanide Manganese Oil Iron Zinc Aluminum Phenol Phosphate Lead	204 3.48 - - 2.89 1.27 2.67 7.8	1,898 7.44 - 3.81 5.87 6.83 29.0	784 5.29 - 3.33 0.4 2.95 4.75 21.9 0.03	784 5.29 0 0 3.30 0.2 2.82
pH (units)	7.7	8.9	8.3	
Average Flow =	3.8 1/s	ec. (60	gpm)	

Constituent	Minimum		Concentrations, mg/l (except as noted)				
		Maximum	Average	Net Average			
uspended Solids	96	104	101	101			
otal Chromium	2.26	2.81	2.52	2.52			
exavalent Chromium	_			0			
otal Cyanide		-	-	Ō			
ree Cyanide		-	-	0			
anganese	0.87	1.45	1.20	1.17			
il	0.4	2.0	1.1	0.9			
ron	0.45	0.83	0.60	0.47			
inc	0.35	1.15	0.84	U.68			
luminum	1.60	3.49	2.57	2.57			
henol	-	-	-	0			
hosphate	0.01	0.01	0.04	0.04			
ead	-	-	-	0			
H (units)	8.0	8.2	8.1				

Table81ANALYTICAL DATA - SP F - PLANT GSLAGPROCESSING DISCHARGE

Constituents	Minimum	Maximum	Average	Net Average
Suspended Solids	26	2,894	1,250	1,250
Total Chromium	0.55	4.54	2.61	2.61
Hexavalent Chromium	0.16	0.45	0.30	0.30
Total Cyanide	-	-	-	0
Free Cyanide	-	-	-	0
Manganese	0.50	10.8	4.14	4.11
Oil	0.8	1.0	1.0	0.8
Iron	0.98	5.33	4.38	4.25
Zinc	0.088	3.36	1.65	1.49
Aluminum	0.27	37.0	14.1	14.1
Phenol	-		-	0
Phosphate	-	_		0
Lead	-	-	-	0
pH (units)	8.4	9.5	8.9	

PLANT H

Chromium metal is produced at this plant by an aluminothermic process using chromium oxide produced by the exothermic reaction of wood flour and sodium dichromate. The production of chromium oxide is not considered here.

The off-gases from the aluminothermic process are cleaned in a unique "wet baghouse" system shown in Figure 15. Water sprays and a wet dynamic scrubber preceed the baghouse and an air heater which raises the gas temperature above the dewpoint to prevent bag clogging. The bags are cleaned by water sprays between each batch-type operation and are dried prior to the next cycle. The waste water effluent contains suspended solids and hexavalent chromium as the principal pollutants.

The waste water is treated batchwise in a series of rubber lined lagoons as shown in Figure 16. There are three reduction basins which each one batch of waste water from the baghouse. Treatment time as treat measured from the filling of the basin to discharge of treated wastewater to the sludge lagoon should take approximately two hours. Two tanks are provided 56,775 liters (15,000 gallon) for treatment flexibility and storage.

Sufficient sulfuric acid addition capacity is provided to lower the waste water pH to about 3.0. At maximum conditions, the daily sulfuric acid requirements are expected to be 454 kg/day (1,000 lbs/day).

Sulfur dioxide added to the waste water through chlorine-type sulfonators is the reducing agent for the treatment process. The theoretical reduction of chromium requires approximately .5 kg (1 lb.) of sulfur dioxide for every kg (2 lb.) of chromates (CrO3) to be reduced. On a daily basis, 136 kg (300 lb.) of SO2 is required.

Upon completion of chemical reduction, sodium hydroxide is added to the basin to raise the pH to form an insoluble chromium hydroxide from the reduced chrome. Approximately 36 kg/day (80 lb/day) of sodium hydroxide is required under maximum flow conditions.

Diffused air agitation is provided to completely mix the reduction basin and to prevent the settling of precipitated solids before the waste water is released to the sludge lagoons. The air supply capacity was based on providing 0.054 cu. m/hr/gal. (0.5 cu. ft./hr/gal.) of waste water to be mixed.

The rubber-lined sludge lagoons have an approximate volume of 1,741,100 liters (460,000 gallons) when gravity flow is used from the reduction basins to the lagoons. Pumping the treated waste water, however, could theoretically utilize the full 3.5 m (11 ft.) depth of the lagoon and would almost triple their capacity. Currently, gravity flow is used, but provisions have been made for the later addition of pumps if needed. Sludge production is expected to approach 454 kg/day (1,000 lb/ day). Approximately six months of sludge storage is provided before removal would be required. This storage capacity will allow for 180 days of continuous operation at the maximum flow and chromium concentrations.

Analytical data from the plant survey are summarized in Tables 82 through 89 for sampling points indicated in Figure 16. The measured temperature rise of the cooling water was 6° C (10.0°F). The cooling pond is designed for a maximum rise of 2.78°C (5°F), and is 61 m X 67 m (200 ft. X 220 ft.).

Figure 15, DIAGRAM OF WET BAGHOUSE SYSTEM

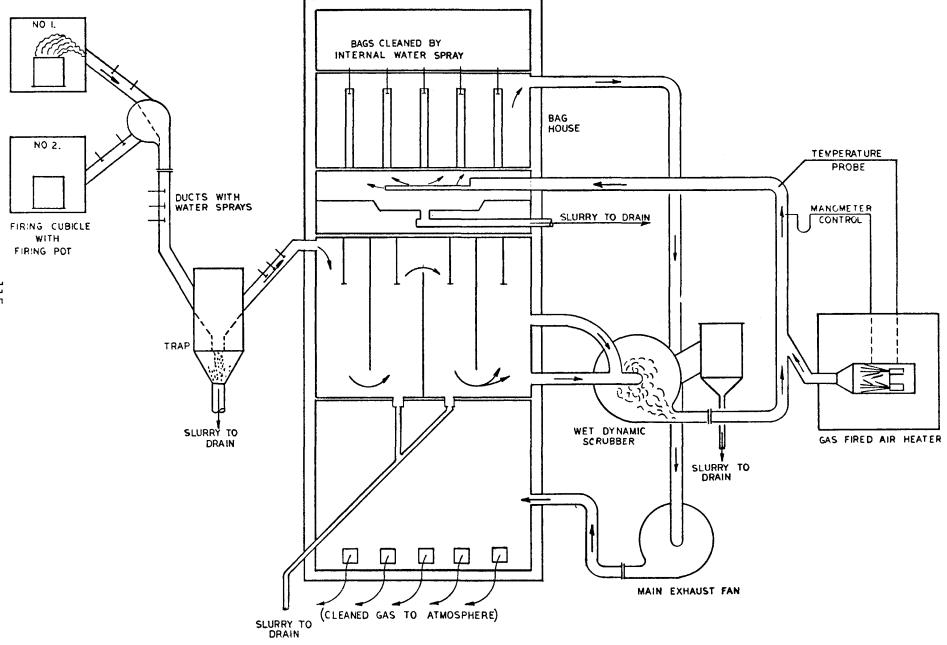
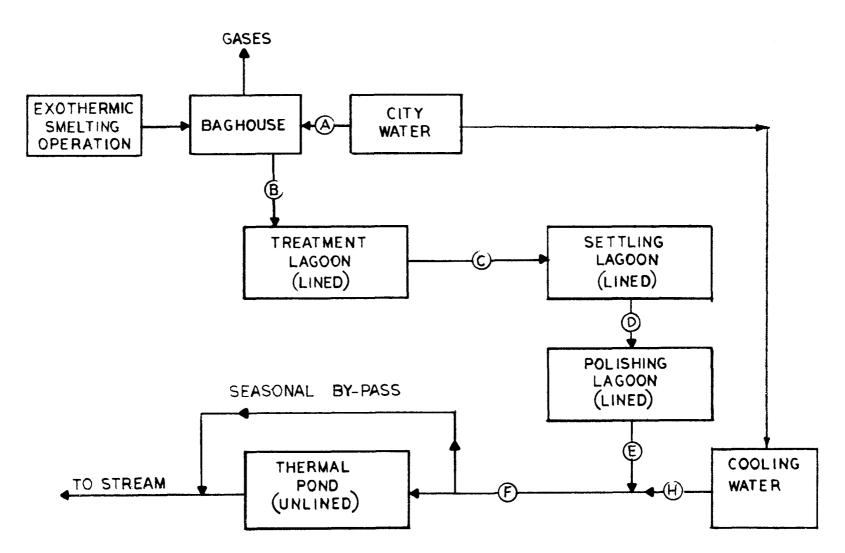


Figure 16. PLANT H WATER AND WASTEWATER SYSTEMS



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	Concentrations, mg/1 (except as noted)				
Constituent	Minimum	Maximum	Average	Net Average	
Suspended Solids	-	-	_	-	
Total Chromium	_	-	-	-	
Hexavalent Chromium	-	-	-	-	
Total Cyanide	-	-	-	-	
Free Cyanide	-		-	-	
Manganese	0.026	0.026	0.026	-	
Oil	-	_	-	-	
Iron	0.22	0.29	0.25	-	
Zinc	0.016	0.016	0.016	-	
Aluminum	-	-	-	-	
Phenol	-	-	-	-	
Phosphate	-	-	-	-	
Lead	-	-	-	-	
pH (units)	5.6	5.7	5.6		

Average Flow = 28.4 l/sec. (450 gpm)

Table 83 ANALYTICAL DATA -SP B- PLANT H BAGHOUSE WASTEWATER DISCHARGE

	Concentr	ations, m	g/l (exce	pt as noted)
Constituents	Minimum	Maximum	Average	Net Average
Suspended Solids Total Chromium	106 101	220 121	136 112	136 112
Hexavalent Chromium Total Cyanide	17	44	37	37
Free Cyanide	-	-	-	0
Manganese	0.040	0.051	0.048	0.022
oil	1.2	2.6	1.8	1.8
Iron	0.04	0.04	0.04	0
Zinc	0.002	0.003	0.002	0
Aluminum	-	-	-	0
Phenol	-	-	-	0
Phosphate	-	-	-	0
Lead	-	_	-	0
pH (units)	12.3	12.4	12.3	

Average Flow = 100,303 1/da (26,500 gal/da)

Table 84 ANALYTICAL DATA -SPC- PLANT H TREATED BAGHOUSE WASTEWATER

Constituent				ot as noted)
	Minimum	Maximum	Average	Net Average
Suspended Solids	674	748	713	713
Total Chromium	114	114	114	114
Hexavalent Chromium	0.047	0.363	0.162	0.162
Total Cyanide		-	-	0
Free Cyanide	-	-	-	0
Manganese	0.41	0.73	0.54	0.51
Oil	0.8	2.0	1.3	1.3
Iron	2.64	3.73	3.27	3.01
Zinc	0.90	1.53	1.27	1.25
Aluminum	127	130	129	129
Phenol	-	-	-	0
Phosphate	0.41	0.50	0.46	0.46
Lead	-	-	-	0
pH (units)	4.7	6.2	5.4	
Average Flow =	100,303 1/	/da (26,500	gal/da)	

Table	85	ANALY	FICAL	DATA	-SPD -	PLANT	Н
	SE	ETTLING	LAGO	ON DIS	SCHARGE		

Constituents	Minimum	Maximum	Average	Net Average
Suspended Solids	58	70	66	66
Total chromium	17.9	18.3	18.1	18.1
Hexavalent Chromium	0.189	0.218	0.208	0.208
Total Cyanide	-	-	-	0
Free Cyanide	-	~	-	0
langanese	0.70	0.70	0.70	0.67
Dil	3.4	3.4	3.4	3.4
Iron	0.24	0.42	0.32	0.06
linc	0.77	0.77	0.77	0.75
Aluminum	31	31	31	31
Phenol	-	-	-	0
Phosphate	0.05	0.05	0.05	0.05
Lead		-	-	0
oH (units)	4.9	4.9	4.9	

Table 86 ANALYTICAL DATA -SPE- PLANT H

	Concentr	ations, m	g/l (exce	pt as noted)
Constituent	Minimum	Maximum	Average	Net Average
Suspended Solids	10	56	38	38
Total Chromium	7.13	7.56	7,40	7.40
Hexavalent Chromium	0.214	0.261		
Total Cyanide	-	-	_	0
Free Cyanide	-	-	-	0
Manganese	0.92	0.92	0.92	0.89
Oil	4.0	4.0	4.0	4.0
Iron	0.17	0.17	0.17	0
Zinc	0.44	0.44	0.44	0.42
Aluminum	15.3	15.3	15.3	15.3
Phenol	-	-	-	0
Phosphate	0.05	0.05	0.05	0.05
Lead	-	-	-	0
pH (units)	5.2	5.2	5.2	
Average Flow =	=0.32 l/s	ec. (5	gpm)	

Table 87 ANALYTICAL DATA -SPF - PLANT H PLANT DISCHARGE

	Concentr	ations, m	g/l (exce	ept as noted)
Constituents	Minimum	Maximum	Average	Net Average
Suspended Solids Total Chromium Hexavalent Chromium Total Cyanide Free Cyanide Manganese Oil Iron Zinc Aluminum Phenol Phosphate Lead pH (units)	- 0.37 0.024 - - 0.22 2.0 0.27 0.023 - - 0.05 5.2	22 0.81 0.090 0.016 0.016 0.40 4.0 0.34 0.074 - - 0.05 6.1	0.009 0.009 0.32 2.7 0.29	6 0.57 0.057 0.009 0.29 1.8 0 0.032 0 0.032 0 0.04 0
Average Flow =	18.9 1/s	ec. (300	gpm)	

Constituent	Minimum			pt as noted) Net Average
conscituent		Maximum	Average	Net Average
Suspended Solids		-	_	_
Total Chromium	-	-		-
Hexavalent Chromium		-	_	-
Total Cyanide	_	-		
Free Cyanide	_	-	-	
Manganese	0.037	0.037	0.037	-
Oil	4.6	4.6	4.6	-
Iron	0.52	0.57	0.55	_
Zinc	0.011	0.011	0.011	
Aluminum	-	-	-	
Phenol	-	-	-	-
Phosphate	0.05	0.05	0.05	
Lead	-	_	-	<u> </u>
pH (units)	5.2	5.3	5.3	

Table 88 ANALYTICAL DATA -SPG- PLANT H PLANT WELL WATER

Taple 89 ANALYTICAL DATA -SPH - PLANT H COOLING WATER

Constituents	Minimum	Maximum		pt as noted) Net Average
Suspended Solids	40	40	40	40
Total Chromium	0.44	0.44	0.44	0.44
Hexavalent Chromium	0.38	0.38	0.38	0.38
Total Cyanide	_	_		0
Free Cyanide	-	-	-	0
Manganese	1.45	1.45	1.45	1.42
Oil	2.2	2.2	2.2	2.2
Iron	1.49	1.49	1.49	1.24
Zinc	0.060	0.060	0.060	
Aluminum	0.27	0.27	0.27	0.27
Phenol	-	-	_	0-
Phosphate	-	-	-	0
Lead		-	-	0
pH (units)	6.0	6.0	6.0	

In Figure 17, a waste treatment scheme is shown in which all of the waste constituents for which guidelines have been developed can be reduced to minimal concentrations. Not all waste streams will contain all constituents and appropriate modifications of this general scheme can be made to reduce costs.

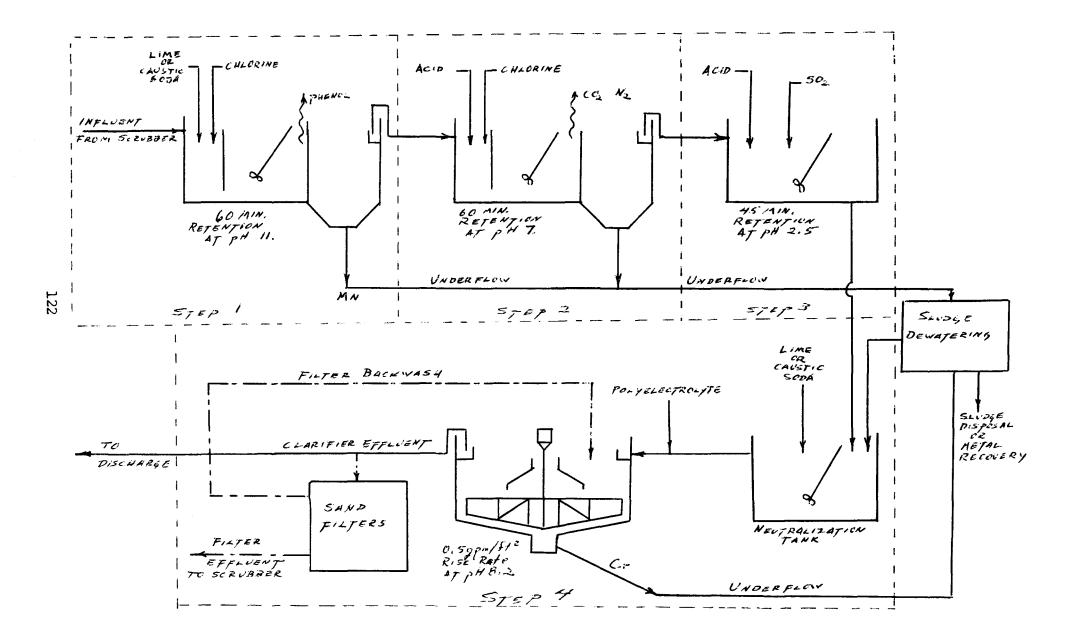
The first step consists of raising the pH of the waste stream to about and the addition of sufficient chlorine to maintain a free residual, 11 followed by sedimentation. In this step, phenol is oxidized, cyanide is oxidized to cyanate, and manganese is precipitated as the hydroxide. In the second step, additional chlorine is added and the pH is lowered to 7.0 by a suitable acid. With a reaction time of 60 minutes, the cyanate is oxidized to CO_2 and N_2 . In the third step, the pH is lowered to 2.5 and sulfur dioxide is added. Allowing a reaction time of 30 minutes, the hexavalent chromium is reduced to trivalent. The fourth step consists of raising the pH to 8.2, adding a polyelectrolyte, and At this point, the trivalent chromium will be allowing sedimentation. removed and final clarification accomplished. With a sufficiently low overflow rate and addition of flocculants in sufficient quantities, an effluent solids concentration of 25 mg/1 of suspended solids can be attained and metals reduced to low levels.

Sand filtration of the final clarifier effluent, with backwash returned to the clarifier, can reduce suspended solids concentrations to 15 mg/l or less. After filtration, the water may be recycled back to the scrubbers.

Obviously, not all plants will require the entire treatment system. For example, plants (such as B or C) producing only manganese or only silicon products in covered furnaces, will require only the first, second and fourth (excluding raising the pH to 8.2) steps of the treatment scheme for removal/destruction of cyanide, phenols, manganese and suspended solids. A plant which specializes in chromium products using open furnaces, would require only the third and fourth steps for reduction of hexavalent chromium and removal of the trivalent and suspended solids. For those plants which produce a variety of products, an alternative solution may be the segregation of wastes and installation of the various treatment modules for chromium reduction, cyanide destruction, etc., to be utilized in series or parallel as required to achieve the proper results. This might result in considerable economies over treatment of all wastes for all parameters.

Some plants which do not have any particular problem with metals or cyanides may be able to use a system similar to that in practice at Plant E, i.e., the addition of flyash from a nearby power station to scrubber waste water, followed by settling. The average suspended solids concentration reached by this system was 15 mg/l. It may be useful to some plants to operate such a system, using existing lagoons, to meet the 1977 standards.





Another alternative solution for 1977 might be the conversion of oncethrough systems to recirculation, with only the blowdown treated for removal of metals (obviously, recirculated water would need to be treated for removal of suspended solids). Since less chemicals would be required for treatment, in addition to smaller tanks, etc., this might result in some savings over the costs estimated in Section VIII.

Some clants may be able to meet the 1977 quidelines simply by modifying their present treatment system somewhat, while some other plants (such as G) seem to meet all the 1977 pollutant load requirements for scrubber For example, both plants C and D appear to meet all but waste water. one of the 30 day average pollutant load requirements for 1977 (manganese and suspended solids, respectively). Plant C should be able to meet fully the 1977 pollutant load standards by some additional treatment for manganese removal prior to clarification. Plant D may be able to rectify the suspended solids load by using more of their clarification capacity (one of their three clarifiers was not operating at the time of our visit), or by making the flow into the clarifiers more quiescent (which may have caused improper distribution of the inlet water), or by backwashing the sand filter more frequently.

Plant B apparently meets all 1977 pollutant load standards but that for suspended solids (in spite of using water on a once-through basis). It is possible that the suspended solids level after the final two settling lagoons (which was not checked) may presently be low enough to meet the standards, but possibly some additional clarification might be necessary. Plant E probably meets the 1977 standard for suspended solids (since the concentration at the outfall was 15 mg/l).

The treatment system as shown in Figure 17 is not utilized in toto in any one plant in the industry. However, the modules which comprise the system are in use in this, or similar, industries.

Plant P, studied as part of the Alloy and Stainless Steel Industry (Ref. 33), utilizes a treatment system for hexavalent chromium reduction, neutralization and clarification almost identical to that shown in steps of This system had an and 4 Figure 17. average influent 3 concentration of about 18 mg/l total chromium and 16 mg/l hexavalent chromium. After treatment, the average concentrations were 0.10 and less than 0.01 mg/l, respectively. This system was operating on a continuous basis. Plant S of the Iron and Steel Industry study (Ref. 35), achieved an average suspended solids concentration of 22 mg/l after clarification of scrubber water from a B.O.F. Plant B achieved 0.22 mg/l cyanide after alkaline chlorination, while concentrations of the phenol level was reduced to 0.50 mg/l. Plant D demonstrates the use of alkaline precipitation of metals and the use of sand filters, although not in a completely optimum manner. The treatment scheme shown may be thought to be based upon the components of all these systems, although as discussed above, any particular plant may not find it necessary to utilize the entire system.

Other treatment methods in use in the industry appear to be relatively ineffective for some constituents. For examples, the relatively high concentrations of suspended solids in the treated water from the clarifier and the sand filter at Plant D has already been discussed, along with suggestions as to the cause for such concentrations. Although flyash treatment appears to work well for removal of suspended solids, as utilized at Plant E, the same treatment has little or no effect on the content of metals found in the effluent. Although the potassium permanganate used at Plant C might be expected to oxidize the cyanide as well as some of the manganese, such was not the case, since the cyanide and manganese concentrations in the overflow were almost as high as in the raw waste. It is possible that higher dosages may more effectively oxidize these wastes, but the cost of such treatment would almost certainly be higher than chlorination. Although the cyanide destruction system was fairly ineffective, this plant stood out in the recirculation and reuse of water from scrubbers and cooling. Some of the blowdown from the cooling tower was used as makeup water for the scrubber system, and 97 percent of the scrubber water was recirculated, the only blowdown being the clarifier underflow.

The control and treatment technologies which have been identified herein are identified as applicable to the various industry categories in Table 90.

Category	Treatment <u>Technology</u>	Description
I	1	Chemical treatment, clarifier-flocculators, recirculation at the scrubber
	2	Chemical treatment, clarifier-flocculators, sand filters and process water recirculation
II	1 2	Chemical treatment, clarifier-flocculators Chemical treatment, clarifier-flocculators, sand filters and process water recirculatio
III	1	Clarifier-flocculators, chemical treatment (if necessary)
	2	Clarifier-flocculators, chemical treatment (if necessary), process water recirculation

Table 90. CONTROL AND TREATMENT TECHNOLOGIES BY CATEGORY

It should be noted that with the exception of the slag processing operations, the raw waste loads and final effluent loads have been calculated in terms of mwhr as the production basis. This was done for the following reasons, after examining the other possible basis (kg (tons)):

1. Uncontrolled emission factors (upon which the raw waste loads depend), are more uniform over the various types of products when expressed as kg (lb/mwhr, rather than as kg/kkg (lb/ton).

2. Power usage is already such a large factor in production costs (about 30 percent) that an increase in power consumption so that the permissible effluent discharge would be higher is very unlikely.

3. Power usage is very well monitored at the furnace itself, usually with a continuous automatic recording device.

4. Furnaces are commonly referred to in the industry as '10 mw' or '35 mw', rather than '50 ton' or '150 ton', as is common practice in the steel industry.

5. The tonnage which may be produced for a given power consumption is fairly wide (factor of 10) and depends on the product, and numerous products can be produced in a given furnace. Use of kg/kkg (lb/ton) as limitations would involve the permit writer in writing a permit with many different conditions. The reader may refer to Table 18 for comparisons of power usage per ton for various products.

Aggregate raw waste loads, representing for some parameters such as chromium and manganese the maximum load which might be expected in the waste, are shown in Tables 91 through 93. The manganese concentrations, for example, would probably only be encountered at these levels from a furnace producing manganese products.

The loads were calculated from flows and concentrations as follows:

load (kg(lb)/mwhr) = mass flow rate of water (kg(lb)/hr) x concentration
+ (10° x furnace power (mw))

load (kg/kkg(lb/ton)) = mass flow rate of water (kg(lb)/hr) x concentration : (amount processed (kkg(tons)/hr) x 10⁶)

Furnace power may be calculated by dividing the number of megawatt-hours used in the furnace in a 24 hour period by 24 hours.

Tables 91-93, describing raw waste and treated effluent loads, have been constructed on the following bases:

Category I - Open Electric Furnaces with Wet Air Pollution Control Devices.

Raw Waste Load - Flow based upon the total water flow in the scrubber [113.6 L/sec (1800 gpm)] rather than effluent water flow at Plant E, sample point G from the scrubber [44.2 L/sec (700 gpm)]. Concentrations of suspended solids and manganese at that sample point adjusted accordingly to compensate for increased flow. Chromium concentrations taken from Plant G, sample point C.

Treatment Level 1 - Concentrations shown are those achievable by the treatment system as shown in Figure 17, less the sand filter and recirculation portions and are generally somewhat higher than those at Plant D, sample point E. Loads are based upon concentrations shown and a water use of 6382 1/mwhr (1686 gal/mwhr).

Treatment Level 2 - Concentrations based on entire treatment system as shown in Figure 17, including the sand filter and recirculation, and are generally somewhat higher than those at Plant D, sample point E. These levels would require better operation of the treatment system than was necessary in Level 1. Loads based upon blowdown rate of 783 1/mwhr (207 gal/mwhr).

Category II - Covered Electric Furnaces and Other Smelting Operations with Wet Air Polluticn Control Devices.

Raw Waste Load - Concentrations and loads as at Plant E, sample point B, except that chromium concentrations are taken from Plant G, sample point C, and manganese concentrations taken from Plant C, sample point C. Loads calculated from Plant B, sample point B, flow.

Treatment Level 1 - Concentrations same as for Category I, treatment level 1, except that cyanide and phenol concentrations are based upon those found at Plant B, sample point D. Loads in kg (lb)/mwhr were calculated using the flows found at Plant B, sample point D.

Treatment Level 2 - Concentrations same as for Category I, treatment level 2, with cyanide concentration based on Plant B, sample point D. Loads in kg (lb)/mwhr based on 1060 l (280 gal)/mwhr being blown down from the recirculation system.

Note: Loads for exothermic and other nonelectric furnace smelting operations based on water usage three times higher (per ton) than for electric furnaces (per mwhr)

Category III - Slag Processing

Raw Waste Load - Maximum of Plant E, sample point I, or sample point D.

Treatment Level 1 - Based on use of clarifier-flocculators.

Treatment Level 2 - Based on recirculation of process water after precipitation of fine suspended solids in clarifier-flocculators. Loads based on a blowdown rate of 5419 l/kkg (1300 gal/ton).

The 24-hour maximums are generally twice the 30 day averages and based upon maximum concentrations found at exemplary plants, or those which might be attained during system upsets or the like. In the case of phencl, the limitations are 1.5 times the 30 day average.

STARTUP AND SHUTDOWN PROBLEMS

There have been no problems of consequence identified in connection with the startup or shutdown of production facilities insofar as waste water control and treatment is concerned. As often as not, scrubber water continues to flow during such periods. There might be some upsets in undersized lagoons or clarifiers used in once-through systems if the water flow is abruptly started after a shutdown. Proper operating procedures can easily handle such occurences and there would be little or no effect in sufficiently large facilities.

Loss of power can effect most of the treatment systems such as chemicals addition for flocculation, cyanide destruction, or chromium reductionprecipitation. In such cases, however, the production process also will stop and little effect on waste water treatment would result.

Table 91 HADUSTRY CATLCORY I OPIN FURNACLS WITH WIT AIR POLLUTION CONTROLS

	Level 1 Effluent									Level 2 Iffluent						
		<i>i Viaste Lo</i>						4 hr Haximum 30 day Avera								
	kg/rwhr	1b/awhr	ng/1	kg/nwhr	lb/rwhr	$\frac{nxj}{1}$	kg/mulir	16/nwhr	nkj/1	kg/mhr	1b/nwirr	mg/1	kg/mhr	15/1.Mir	$\frac{ng}{1}$	
Suspended Solids	24.0	52.8	1460	.160	.352	25.	.319	.703	50.	.012	.026	15.	.024	.052	30.	
Total Chronium	•078	.172	4.76	.0032	.007	.5	.006	.014	1.	.0004	.0009	.5	.0008	.0017	1.	
Hexavalent Chromium	.005	.012		.0003	.0007	.05	.0006	.0014	.1	.00004	.0001	.05		.0002	.1	
Manganese	10.07	22.17	613	.032	.070	5.	.064	.141	10.	.0039	.0086	5.	.008	.017	10.	
	7	/alue				Value						Valu	<u>16</u>			
pH		7.2				6.0 - 9.	0					6.0·-	9.0			
	1/m/hr	gal/nwhr		<u>1</u> ,	mwhr		gal/	whr		-	l/rwhr		a	al/mwhr		
Flow	16,410	4335		6	382		1686				783			207		

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Table ⁹² INDUSTRY CATEGORY II COVERED ELECTRIC FURNACES AND OTHER SMELTING OPERATIONS WITH WET AIR POLLUTION CONTROL DEVICES

				Level I Effluent							Level 2 Effluent						
	Raw Waste Load 30 Day Average				ige	24 hr Maximum 30			30	30 Day Average 24			hr Maximum				
	kg/nwhr	1b/mwhr	mg/1	kg/nwhr	1b/mwhr	mg/l	kg/mwhr	lb/mwhr	mg/1	kg/mwhr	1b/mwhr	mg/1	kg/mwhr	lb/nwhr	mg/1		
Suspended Solids	13.02	28.67	1555.	0.209	0.461	25.	0.419	0.922	50.	0.016	0.035	15.	0.032	0.071	30.		
Total Chromium	0.040	0.088	4.76	0.004	0.009	0.5	0.008	0.018	1.0	0.0005	0.0012	0.5	0.001	0.002	1.0		
Hexavalent																	
Chromium	0.003	0.006	0.32	0.0004	0.0009	0.05	0.0008	0.0018	0.1	0.00005	0.0001	0.05	0.0001	0.0002	0.10		
Total Cyanide	0.021	0.046	2.49	0.002	0.005	0.25	0.004	0.009	0.5	0.0003	0.0006	0.25	0.0005	0.001	0.5		
Manganese	3.74	8.24	447.	0.042	0.092	5.0	0.084	0.184	10.	0.005	0.012	5.	0.011	0.023	10.		
Phenol	0.061	0.134	7.27	0.004	0.009	0.5	0.006	0.013	0.7	0.0002	0.0005	0.2	0.0004	0.0009	0.4		

	gal/mwhr	1/mwhr	gal/mwhr	1/mwhr	gal/mwhr	1/mwhr			
Flow	2210	8365	2210	8365	280	1060			
	Valu	e		Value	Value				
pH	6.0-9.	0		6.0-9.0	6.0-9.0	6.0-9.0			

Table 93 INDUSTRY CATEGORY III SLAG PROCESSING

······································	Level 1 Effluent										Level 2 Effluent							
	Raw Waste Load 30 Day Average						24 hr	24 hr Maximum			30 Day Average 24 hr Ma				aximum			
	kg/kkg processed	lb/ton processed	mg/1	kg/kkg processed	lb/ton processed	mg/1	kg/kkg processed	lb/ton processed	<u>mq/1</u>	kg/kkg processod	lb/ton processed	<u>1 mq/1</u>	kg/kkg processed	lb/ton processed	<u>mg/1</u>			
Suspended Solids Total Chronium Manganese	46.0 0.109 2.87	91.9 0.217 5.74		1.330 4 0.026 0.266	2.659 0.053 0.532	25. 0.5 5.	2.659 0.053 0.532	5.319 0.106 1.064	50. 1. 10.	0.136 0.0027 0.027	0.271 0.0054 0.054	25. 0.5 5.	0.271 0.0054 0.054	0.542 0.011 0.108	50. 1. 10.			
	Value					alue												
pII	6.2					6.0 - 9.0				6.0 - 9.0								
	1/kkg	gal/ton			1/kkg			gal/ton			<u>1/kkg</u>		<u>1</u>	b/ton				
Flow	53,100	12,750			53,100			12,750			5419			1300				

SECTION VIII

COST, ENERGY AND NONWATER QUALITY ASPECT

Capital and operating cost information was obtained from each plant surveyed. The capital costs (per mw capacity) for water treatment systems at the plants surveyed varied from \$5,581 (for an extensive lagooning system with a clarifier) to \$21,760 (for a treatment and recirculation system). Operating costs varied from a low of \$0.010/mwhr (for settling ponds) to a high of \$0.652/mwhr (for a treatment and recirculation system).

Capital costs are given in terms of installed capacity and operating costs in terms of units of production and also in terms of waste water flows. These costs were based upon cost of capital at an interest rate of 8 percent, and a depreciation period of 15 years.

Capital costs have been adjusted to August, 1971 dollars using the Chemical Engineering Plant Cost Index (1957-59=100). This index has been indicated by a consultant to The Ferroalloys Association to be best indicative of cost changes in the industry. Operating costs have been adjusted when necessary on the basis of an average of 3.5 percent per year.

Power costs were calculated on the basis of flow rates and pumping head, and have been assumed at one cent per kwhr, which is the cost used in the EPA-TFA Air Pollution Study (Ref. 32). This estimate has been confirmed by The Ferroalloys Association as being equal to the average cost in the industry.

The cost of land was not included as part of the total investment, since it is thought that very few (if any) plants will need to purchase land for wastewater treatment. Of the seven plants which were visited which used some type of wet air pollution control system, six were sampled and are discussed in Section VII. Three of the plants which were visited had multi-acre lagoon systems, which could either be utilized as part of wastewater treatment system, or used for landfilling sludge. The other four plants had varying degrees of treatment systems presently in use. Those two which appeared to have the least amount of land available, are in such position as to already meet all (or most of) the standards. The remaining two plants appeared to have sufficient land so as not to require the purchase of additional land. The treatment system at Plant D, for example, was housed in a building about $50 \cdot x 100$ with two lagoons totalling about another $50 \cdot x 100$. Being generous, this would give a total land requirement of about a third of an acre. Therefore, it is not anticipated that the cost of acquiring land for those few plants which may require it would add more than \$2,000 to the total investment cost. Additionally, the cost would be for the entire plant, not merely per mw of capacity, so that for a small, 20 mw plant, the added investment for land would probably be less than 1 percent of the cost of the treatment system.

The following bases were used for cost calculations by Category and Treatment Level:

Category I, Treatment Level 1.

Costs were developed for the treatment system as shown in figure 17, on the basis of a 63.1 l/sec (1000 gpm) flow rate. At a water use of 6362 l/mwhr [1686 gal/mwhr], this is equivalent to the flow rate from a furnace operating at 35 mw. The costs include mechanical equipment, tanks, piping, valves, electrical, engineering, installation, etc. They are based upon the complete system less the sand filter and recirculation and may, therefore, be somewhat high, since a particular plant may not require all the treatment steps. The investment costs will probably be less (per mw) for a plant larger than the model, and greater for a plant smaller than the model.

Operating and maintenance costs at this level of estimation are best figured as a percentage of capital costs for similar type plants. The "Inorganic Chemicals Industry Profile" indicated for 59 plants surveyed operating costs per annual unit of production equal to 28 percent of the capital cost per annual unit of production. The operating costs at Plant C are equal to 23.4 percent per year of the capital cost. The operating costs at Plant D are equal to 23.0 percent of the capital cost. The operating costs at Plant B are equal to 30.9 percent per year of the capital costs. Operating costs are thus estimated on the basis of 30 percent per year of the estimated capital cost, prorated as at Plant C.

Category I, Treatment Level 2.

Costs expanded from Level 1, above, to include costs of recirculation and sand filtration, with a proportionate increase in annual and operating costs.

Category II, Treatment Level 1.

Costs were developed as for Category I, Level 1. 63.1 1/sec (1000 gpm) at a use comparable to that at Plant B, sample point B, (8365 1/mwhr [2210 gal/mwhr]), is equivalent to the flow from a furnace operating at 27 mw. As before, the investment cost per mw will be somewhat higher for small plants and less for large plants.

Category II, Treatment Level 2 and 3.

Same as for Category I, Level 2, but based on 27 mw furnace.

Category III, Treatment Level 1.

Costs were calculated for two clarifier flocculators, with the necessary piping, pumps and other appurtenances. Costs were based upon the use of 53,148 l/kkg (12,750 gal/ton) processed.

Category III, Treatment Level 2.

Costs are greater than for Level 1 by the addition of pumps and pipes necessary for recycle.

The costs for each are summarized in Tables 94 and 95.

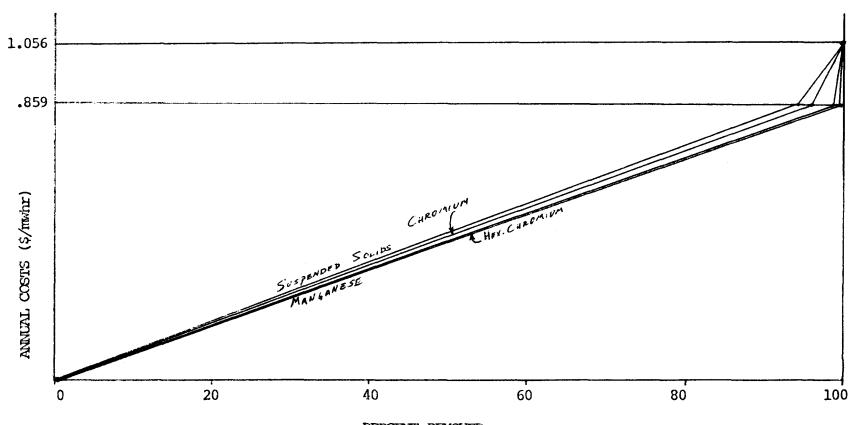
Figures 18 through 20 show the relative costs of treatment for reduction of effluent loads of the critical pollutants from the raw wastes. These curves provide graphical information of interest, but must be read in the context of the previously described Treatment Levels to be of value.

······································		Annual Costs (\$ per mwhr or ton)							
Inudstry Category and Treatment Level	Investment (\$ per mw or tpd)	Capital	Depreciation	Operating Cost less Power	Power	Total			
Category I: Treatment Level 1 Treatment Level 2	17,143 21,063	0.103 0.127	0.138 0.169	0.606 0.745	0.012 0.015	0.859 1.056			
Category II: Treatment Level 1 Treatment Level 2	22,222 27,303	0.134 0.165	0.178 0.219	0.785 0.965	0.016 0.019	1.113 1.368			
Category III: Treatment Level 1 Treatment Level 2	2.526* 2,604*	0.344* 0.357*	0.459* 0.485*	0.421* 0.421*	0.051* 0.051*	1.28* 1.31*			

Table 94. TREATMENT LEVEL COSTS ON UNIT OF PRODUCTION BASIS (costs on basis of mw and mwhr unless noted thus*)

Table 95. Treatment Level Costs on Wastewater Flow Basis

		An	nual Costs (\$ p	er 1,000 gal)		
Industry Category and Treatment Level	(\$ per gpm)	Capital	Depreciation	Operating Cost less Power	Power	Total
Category I:						
Treatment Level 1	600	0.057	0.076	0.336	0.007	0.476
Treatment Level 2	737	0.070	0.094	0.413	0.008	0.585
Category II:						
Treatment Level 1	600	0.057	0.076	0.336	0.007	0.476
Treatment Level 2	737	0.070	0.094	0.413	0.008	0.585
Category III:						
Treatment Level 1	285.29	0.027	0.036	0.033	0.004	0.100
Treatment Level 2	294.12	0.028	0.038	0.033	0.004	0.103



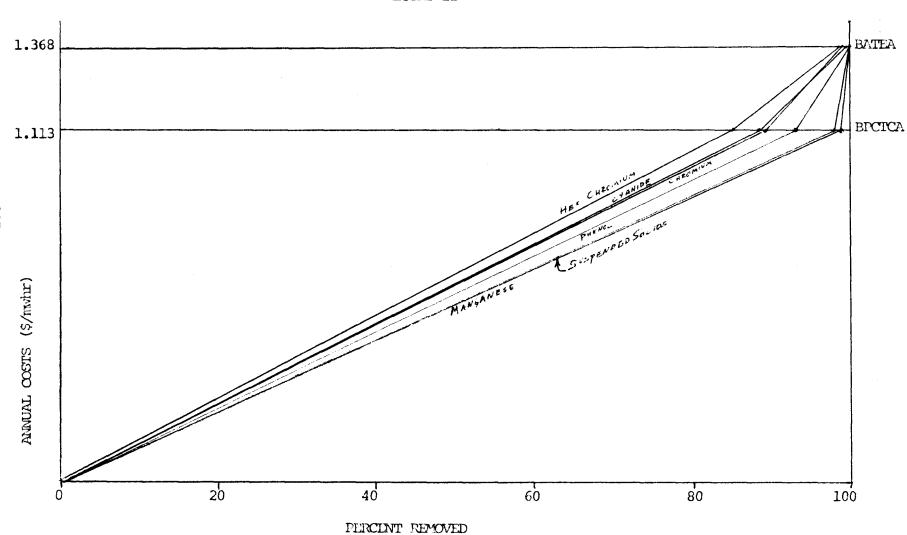
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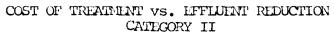
FIGURE 18.

COST OF TREATMENT vs. EFFLUENT REDUCTION CATEGORY I

PERCENT REMOVED







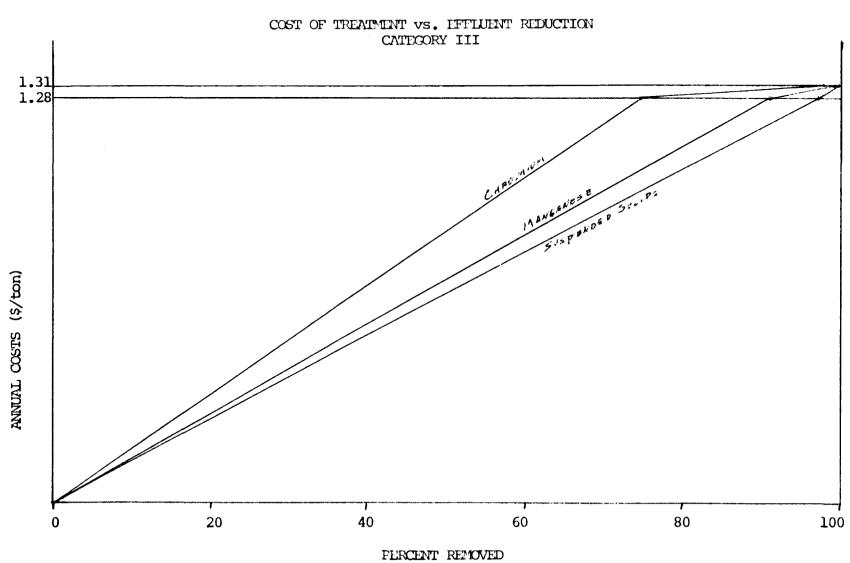


FIGURE 20.

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INCREMENTAL COSTS OF ACHIEVING LEVELS OF TREATMENT TECHNOLOGY

The cost of achieving the various levels of treatment technology in the industry will vary from plant-to-plant, depending upon the treatment currently in use. The best estimates of these costs are given below by Category, based upon the assumed levels of present technology in "typical" plants.

Category I

The "typical" plant probably has a lagoon in which the scrubber wastewater is treated by plain sedimentation prior to discharge. Although this 'typical' lagoon may be usable as part of a new treatment scheme, it is likely that almost all of the costs shown in Table 94 would be incurred to bring the plant's effluent down to the suggested limitation. If the plant were to go to Level 2 from this base, it would require only the addition of a sand filter and recirculation system, i.e., the arithmetic difference in costs between Levels 1 and 2. Therefore, the incremental cost of reaching Level 1 would be \$17,143/mw in investment, and \$0.859/mwhr in annual costs. The additional cost of reaching Level 2 would be \$3,920/mw for investment, and \$0.197/mwhr in annual costs.

Category II

The "typical" plant probably has a lagoon in which the scrubber waste water is treated by sedimentation and for destruction of cyanides prior to discharge. Again, it may be assumed that the cost of reaching Level 1 is 100 percent of that shown, and the cost of reaching Level 2 from Level 1 is the arithmetic difference. Therefore, the incremental cost of reaching Level 1 would be \$22,222/mw in investment, and \$1.113/mwhr in annual costs. The additional costs to reach Level 2 would be \$5,081/mw in investment, and \$0.255/mwhr in annual costs.

Category III

The "typical" plant again for this Category probably has a small lagoon and would probably require expenditure of 100 percent of the costs shown, which makes the incremental cost for Level 1 \$2,526/tpd for investment, and \$1.28/ton for annual costs. To reach Level 2 would require an additional investment of \$78/tpd, and increase annual costs by \$0.03.

ENERGY AND NON-WATER QUALITY ASPECTS

There are significant energy and nonwater quality aspects to the selection and operation of treatment systems. These may be considered as land requirements, air and solid waste aspects, by-product potentials, and energy requirements.

Land Requirements

One of the important aspects in the selection of wastewater treatment systems in this industry is the land required for water treatment systems. Many plants in this industry have extensive land areas available for such uses and may elect to use this land, and existing lagoons, as part of their water treatment system. Other plants might possibly not have land readily available and would have to select alternative treatment systems such as the use of filters for sludge dewatering, rather than sludge lagoons, for this reason alone.

Air and Solid Wastes

The solid waste produced by treatment of waste waters in the industry derives principally from the smelting operation as waste from air pollution control devices. The solid waste from air pollution controls produced whether a dry or wet system is utilized and varies only in is that the former produces a slurry or sludge, the latter a fine dust. The slurry or sludge is generally accumulated in sludge lagoons, while the dry dust may be bagged and landfilled or simply piled. More careful attention should be directed to the disposal of these potentially harmful materials. Possible improvements might be landfilling in a sealed site, or encapsulation in concrete or polymers. There has been little success in efforts to agglomerate these solids for recharging to the smelting furnaces, although it is probable that dry dust could be utilized more easily than wet sludge.

By-Product Potentials

In the case of metals refining at one plant, a baghouse is to replace a wet scrubber and the particulate matter is to be leached to produce the electrolyte for electrolytic manganese production. The potential for such recovery methods is probably very limited, since this refining process is not a common operation. Although there has been some discussion in the industry of reusing the particulates collected in baghouses as part of the furnace charge, to the best of our knowledge this has not actually been attempted as yet.

Slag concentration is used at a number of plants to recover metal values and as a by-product, to produce slag for sale or other use. The sale or use of slag varies from place to place. In one location slag can be readily sold at a good price, since stone must be imported from a distance. This is probably not a common situation. At another plant all of the slag produced is used on-site for road building. At other plants, markets or uses for slag cannot be found.

By-product recovery in the case of the further use of the metals refining particulates reduces a solid waste problem and does not add to potential water pollution, since the particulates replace ore in an electrolytic process. Slag concentration reduces solid wastes, but results in a water pollution potential not otherwise present.

Energy Requirements

The use of recirculation cooling water systems is primarily due to water supply limitations. Plants that use well water supplies generally do not have enough water for once-through cooling systems. Those which use purchased city water find that water costs favor recirculating systems.

Power requirements for waste water treatment systems are generally low. Power uses range from less 0.07 percent to 1.3 percent of the power used in the smelting furnaces. The higher figure is for the most powerintensive system found during the survey, which uses clarifierflocculators, sand filters, softening, and recirculation of process water. The lower figure is for a system using lagoons, a clarifierflocculater, and recirculation. This compares with the use of about 10 percent of the productive power for operation of high-energy scrubbers for air pollution control.

Monitoring

For the purpose of writing a permit, one would need to know historical production figures for the plant. These may be in the form of tonnage of the various products (broken down by product, and also by the type of furnace and air pollution control system), or else in the form of power consumption, broken down by the type of furnace and air pollution control system.

For example, Plant X may have produced 200 tons per day of HC ferromanganese in open electric furnaces with wet scrubbers, 150 tons per day of silicomanganese in a covered electric furnace with a wet scrubber, and 350 tons per day of 50 percent ferrosilicon in furnaces with dry or no air pollution control equipment. These tonnage figures may then be converted, using Table 18, into power consumption figures.

As another example, Plant Y may have used 110 mwhr/day in open furnaces with wet air pollution control systems, 290 mwhr/day in a covered furnace with a wet scrubber, and 480 mwhr/day in furnaces with baghouses.

An alternative for plants which do not posses historical production data, would be the use of capacity figures, such as the furnace or transformer rating.

Historical data covering a year's time would probably be necessary, although in the case of a plant which has several furnaces out of operation, but plans to use these in the future, a longer period might be necessary.

Once the permit has been issued, the plants would need to know the appropriate flows and concentrations of the pollutant parameters so that the pollution load from the plant may be reported as lb/day.

SECTION IX

BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE, GUIDELINES AND LIMITATIONS

INTRODUCTION

The effluent limitations which must be achieved by July 1, 1977 are to specify the degree of effluent reduction attainable through the application of the Best Practicable Control Technology Currently Available. This is generally based upon the average of the best existing plants of various sizes, ages and unit processes within the industrial category and/or subcategory.

Consideration must also be given to:

a. The total cost of application of technology in relation to the effluent reduction benefits to be achieved from such application:

b. the size and age of equipment and facilities involved;

c. the processes employed;

d. the engineering aspects of the application of various types of control techniques;

e. process changes;

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

Also, Best Practicable Control Technology Currently Available emphasizes treatment facilities at the end of a manufacturing process but includes the control technologies within the process itself when the latter are considered to be normal practice within an industry.

A further consideration is the degree of economic and engineering reliability which must be established for the technology to be "currently available." As a result of demonstration projects, pilot plants and general use, there must exist a high degree of confidence in the engineering and economic practicability of the technology at the time of commencement of construction or installation of the control facilities.

Definition of what constitutes 'best practicable' technology for many industries involves, at first, a general review of the industry to determine the best technologies being practiced in the industry. Then, after closer review and investigation of these technologies, the 'best practicable' technology would be assessed as the average of the best, though not necessarily the best technology, after taking into account information relating to other factors spelled out in the Act. In those industries where present treatment is uniformly inadequate, a higher degree of treatment than is presently practiced may be required, based on a comparison with existing treatments for similar wastes in other industries. Factors for determining the 'best available' technology are similar, except that rather than assessing the average of the best, the focus is on the very best technology currently in use or demonstrably achievable.

Under this analysis of the statutory standard, it is the opinion of the Agency that it is not necessary that 'best practicable' technology be currently in use as a single treatment.

EFFILENT REDUCTION ATTAINABLE THROUGH THE APPLICATION OF BEST PRACTICAELE CONTROL TECHNOLOGY CURRENTLY AVAILABLE (BPCTCA)

Based upon the information contained in Sections III through VIII of this report, a determination has been made that the degree of effluent reduction attainable through the application of the best practicable technology currently available is the application of the levels of treatment described in Section VII as the Level 1 technologies to the various industry categories as shown in Table 96.

Table 96. BPCTCA EFFLUENT GUIDELINES TREATMENT BASIS

<u>Industry Category</u>	Treatment Basis
I	Chemical treatment, clarifier-flocculators, recirculation at the scrubber
II	Chemical treatment, clarifier-flocculators
III	Clarifier-flocculators

Category I

New, larger open furnaces have generally been equipped with high-energy scrubbers when wet air pollution controls have been selected. The water use at the scrubber is high due to the volume of the off-gases to be treated, but the waste water effluent volume is reduced by recirculation at the scrubber and this lowered volume is that to be treated for discharge. The costs here would be those given in Tables 94 and 95, Category I, Treatment Level 1. The alternative use of steam/hot water scrubbers or electrostatic precipitators should result in even less costs if treatment is for discharge, since waste water volumes would be less.

Although the entire treatment system is not presently in use at any one plant, portions of the suggested technology as shown in Figure 17 are readily transferable from other plants within this or similar industries. No innovative or new technology is involved - rather, the application of existing and fairly pedestrian technology to this industry's problem.

Category II

Covered furnaces have generally been equipped with disintegrator scrubbers in the past, although some of the newer furnaces are equipped with high energy scrubbers. The volume to be treated for discharge was taken as that of Plant B, sample point D. As in Category I, the usage of steam/hot water scrubbers should significantly reduce treatment costs, since water volumes would be less.

Although the technology is not in use at any one plant, portions are in use at various plants and should be readily transferable.

Category III

The loads attainable by the use of such technology described as Level 1 for this category are probably as good as could be expected if water is used on a once-through basis. The technology of clarification and rather commonplace. methods Other flocculation is, again, for sedimentation (such as lagoons) might be used for meeting the recommended quidelines, if sufficient land is available. The suggested technology, however, minimizes land requirements.

Summary

The suggested Guidelines do not appear to present any particular problems in implementation. The processes involved are all in present use in ferroalloy plants, are cormon waste water treatment methods and no engineering problems are involved in design or construction. Process changes are not required in any existing plants and the size or age of facilities has little or no bearing on the applicability of these methods.

Some additional solid wastes are generated by the suggested treatment methods since better treatment than is presently practiced is proposed. Power consumption for treatment is about 1 percent of that used in the furnaces.

The effluent limitations here apply to measurements taken at the outlet of the last waste water treatment process unit.

The effluent loads, together with estimated costs applicable to the Best Practicable Control Technology Currently Available Guidelines and Limitations are summarized in Table 97.

APPLICATION OF LIMITATIONS

The application of these guidelines and performance standards to specific plants is intended to be on the basis of a "building block" approach to define the effluent limits from the plant as a whole. Consider, for example, a ferroalloy plant with the following processes:

30 mw open furnace with an electrostatic precipitator with water sprays 20 mw open furnace with a baghouse 15 mw covered furnace with a scrubber Slag concentrating, feed rate 9.07 kkg (10 tons)/hr Exothermic smelting, producing 4.54 kkg (5 tons)/day.

The total permissible 30 day average load of suspended solids would be calculated by Category as follows:

Category I: (30 X 24) mwhr/day X 0.352 lbs/mwhr = 254 lbs/day

Category II: (15 X 24) mwhr/day X 0.461 lbs/mwhr = 166 lbs/day 5 ton/day X 3 X 0.461 lb/ton product = 7 lb/day

Category III: 10 ton/hr X 24 hr/day X 2.659 lb/ton processed = 638 lb/day

Total plant load, lb/day suspended solids = 1,065 lbs/day (484 kg/day)

	CATEGORY I 30 Day Average 24 hr Maximum				30 Day	CATEGORY III 30 Day Average 24 hr Maximum						
		lb/m/hr		lb/rwhr	kg/mvnr	1b/nwir	24 hr M kg/nwhr	1b/hwnr	kg/kkg	lb/ton	kg/kkg	lb/ton
Suspended Solids Total Chromium Nexavalent	.160 .0032	.352 .007	.319 .006	.703 .014	.209 .004	.461 .009	.419 .008	.922 .018	1.330 .026	2.659 .053	2.659 .053	5.319 .106
Chromium Manganese Total Cyanide Phenol	.0003 .032	.0007 .070	.0006 .064	.0014 .141	.0004 .042 .002 .004	.0009 .092 .005 .009	.0008 .084 .004 .006	.0018 .184 .009 .013	.266	•532	.532	1.064
pH		6.0 -	9.0			6.0 -				6.0	- 9.0	
Cost Item	\$/mw	\$/mwhr			\$/17K-1	<u>\$/n</u> 1	<i>vhr</i>		\$/ton/	'day	\$/ton	
Investment Capital Costs Depreciation Operating Costs	17,143	0.103 0.138			22,222	0.13			2,526		0.344 0.459	
Less Pover Power Costs Total Operating		0.606 0.012				0.78 0.01					0.421 0.051	
Costs		0.859				1.13	L3				1.28	

Table 97. HEST PRACTICABLE CONTROL TECHNOLOGY CURRINTLY AVAILABLE GUIDELINES AND LINTTATIONS

*For nonelectric furnace smelting operations, read units as kg/kkg (lb/ton), rather than kg/nwhr (lb/nwhr), and multiply the metric unit limitations by 3.3 and the English unit limitations by 3.0.

SECTION X

BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE, GUIDELINES AND LIMITATIONS

INTRODUCTION

The effluent limitations which must be achieved by July 1, 1983 are to specify the degree of effluent reduction attainable through the application of the Best Available Technology Economically Achievable (BATEA). BATEA is determined by the very best control and treatment technology employed by a specific point source within the industry category or by technology which is readily transferable from another industrial process.

Consideration must also be given to:

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 the application of this level of technology;

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

Also, Best Available Technology Economically Achievable assesses the availability of in-process controls as well as additional treatment at the end of a production process. In-process control options include water re-use, alternative water uses, water conservation, by-product recovery, good housekeeping, and monitor and alarm systems.

A further consideration is the availability of plant process changes and control techniques up to and including "no discharge" of pollutants. Costs for this level of control are to be the top-of-the-line of current technology subject to engineering and economic feasibility.

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

Based upon the information contained in Sections III through VIII of this report, a determination has been made that the degree of effluent

reduction attainable through the application of best available technology economically achievable is the application of the levels of treatment described in Section VII as Level 2 to the various industry categories as shown in Table 98.

Table 98. BATEA EFFLUENT GUIDELINES TREATMENT BASIS

است اس بین های است است بین میکند. بین میکن برای میکن با این میکن بین میکن و بین میکن میکن میکن میکن میکن میکن است کار این	
Industry Category	<u> </u>
I	Chemical treatment, clarifier-flocculators, sand filters, recirculation
II	Chemical treatment, clarifier-
III	flocculators, sand filters, recirculation Clarifier-flocculators, recirculation

These guidelines have been selected on the basis of the following considerations and assumptions.

Category I

The effluent load reduction above Level 1 is primarily due to the effluent reduction attained through recirculation of the scrubber water, although some of the reduction is due to lower concentrations in the effluent. Portions of the technology described are in use at various ferroalloys plants, and no new or innovative technology is required.

Consideration was given in Category I to the replacement of existing scrubbers with fabric filter collectors, which would result in zero discharge of pollutants. However, the large investment costs required (from \$1.19 to 2.34 million for a 30 mw furnace vs approximately \$.632 million for a scrubber waste water treatment system) probably makes this technology economically unachievable, particularly so when it would cause the premature retirement of existing air pollution control systems. Additionally, some plants may not find baghouses to be the most efficient or economical means for reduction of air emissions.

Category II

Again, load reduction above Level 1 is due primarily to the reduction in effluent volume attained by recirculation. Although Plant C was achieving 97 percent recirculation of the scrubber water, this high a proportion may not be feasible for all plants and the standard was so selected. As before, no innovative technology is required.

Category III

Since water is used only as a transport or cooling medium in slag processing, the quality of recirculated water is of importance only to the extent of its abrasiveness on valves and pumps. Operation with minimal discharge (less than 2 percent) of total circulation is practiced at one plant. However, since differing conditions may require greater blowdown rates, a higher blowdown rate has been used to calculate the guidelines. It is intended that removal of suspended solids be accomplished prior to recirculation, so that valves, etc. will not be unduly abraded. The engineering problems are minimal, requiring only recirculation pumps and clarifier-flocculators close to the slag processing equipment.

Summary

The suggested Guidelines present no particular problems in implementation from an engineering aspect and require no process changes. Water reuse and good housekeeping are emphasized. Age of equipment and facilities are of no particular importance.

additional solid wastes of significance are created by the suggested No treatment methods. Increased power consumption may amount to as much as 1.3 percent of furnace power in the most energy intensive water treatment system. The effluent limitations here apply to measurements taken at the outlet of the last waste water treatment process unit. It not judged to be practical to require the treatment or control of is runoff due to storm water for the 1983 standards for existing plants. Such treatment or control would be very difficult to accomplish in older plants having many years of accumulations of slag, collected airborne particulates, etc. Depending upon the geography of a plant site and the acreage involved, costs would vary widely from plant to plant. Some containment as earthen dikes around production areas could such conceivably be used. In one steel mill where it was proposed to collect runoff and treat the collected water in a lagoon, the costs involved to the total expenditures for a minimum discharge equal were recirculation system.

The effluent loads, together with estimated costs, applicable to the Best Available Technology Economically Achievable Guidelines are summarized in Table 99.

APPLICATION OF LIMITATIONS

The application of these guidelines and performance standards to specific plants is intended to be on the basis of a "building block" approach to define the effluent limits from the plant as a whole. The application is as illustrated under Best Practicable Control Technology Currently Available in Section IX, except that with Best Available Technology Economically Achievable, the permissible suspended solids load for the hypothetical plant would be 97 lb/day (44 kg/day), rather than 1,065 lb/day.

		CATE	GORY I			CATE	GORY II*		CATEGORY III				
	30 Day Average 24 hr Maximum			30 Day	30 Day Average 24 hr Maximum				30 Day Average 24 hr Maximum				
	kg/mwhr	1b/mwhr	kg/mwhr	1b/mwhr	kg/mwhr	1b/mwhr	kg/mwhr	1b/mwhr	kg/kkg processed	lb/ton processed	kg/kkg processed	lb/ton processed	
Suspended Solids Total Chromium Hexavalent	.012 .0004	.026 .0009	.024 .0008	.052 .0017	.016 .0005	.035 .0012	.032 .001	.071 .002	.136 .0027	.271 .0054	.271 .0054	.542 .011	
Chromium Total Cyanide	.00004	.0001	.00008	.0002	.00005	.0001 .0006	.0001	.0002 .001					
Manganese Phenol	.0039	.0086	.008	.017	.005 .0002	.012 .0005	.011 .0004	.023 .0009	.027	.054	.054	.108	
pH	6.0-9.0				6.0-9.0				.6.0-9.0				
Cost Item	\$/mw	\$/mwh	<u>r</u>		y/mw	\$/mwhr			\$/ton/yr	<u>\$/tc</u>	n		
Investment	21,063				27,303				2,604				
Capital Costs		0.127			-	0.165			-	0.35	7		
Depreciation		0.169				0.219				0.48	5		
Operating Costs Less Power		0.745				0.965				0.42			
Power Costs		0.015				0.019				0.05	1		
Total Operating Costs		1.056				1.368				1.31			

Table 99 BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE GUIDELINES AND LIMITATIONS

*For non-electric furnace smelting operations, read units as kg/kkg (lb/ton), rather than kg/mwhr (lb/mwhr) and multiply the metric unit limitations by 3.3 and the English unit limitations by 3.0.

SECTION XI

NEW SOURCE PERFORMANCE STANDARDS AND PRETREATMENT STANDARDS

INTRODUCTION

The effluent limitations which must be achieved by new sources, i.e., any source, the construction of which is started after publication of new source performance standard regulations, are to specify the degree of treatment available through the use of improved production processes and/or treatment techniques. Alternative processes, operating methods or other alternatives must be considered. The end result is to identify effluent standards achievable through the use of improved production processes (as well as control technology). A further determination which must be made for new source performance standards is whether a standard permitting no discharge of pollutants is practicable.

Consideration must also be given to:

- a. the type of process employed and process changes;
- b. operating methods;
- c. batch as opposed to continuous operation;
- d. use of alternative raw materials and mixes of raw materials;
- e. use of dry rather than wet processes;
- f. recovery of pollutants as by-products.

In addition to recommending new source performance standards and effluent limitations covering discharges into waterways, constituents of the effluent discharge must be identified which would interfere with, pass through or otherwise be incompatible with a well designed and operated publicly owned activated sludge or trickling filter waste water treatment plant. A determination must be made as to whether the introduction of such pollutants into the treatment plant should be completely prohibited.

EFFLUENT REDUCTION ATTAINABLE THROUGH THE APPLICATION OF NEW SOURCE PERFORMANCE STANLARDS

Based upon the information contained in Section III through VIII of this report, a determination has been made that the degree of effluent

reduction attainable by new sources is the same achieved by application of the levels of treatment described in Section X and as shown in Table 100.

Table 100. NEW SOURCE PERFORMANCE STANDARDS EASIS

Treatment Basis
hemical treatment, clarifier -
locculators, sand filters, recirculation. hemical treatment, clarifier -
locculators, sand filters, recirculation. larifier-flocculators, recirculation

These performance standards have been selected on the basis of the following assumptions and considerations:

Category I

Although baghouses may be used for air pollution control, because of energy, efficiency and cost considerations some plants may elect to use various 'wet' systems, such as steam/hot water scrubbers or electrostatic precipitators. Therefore, the treatment specified for BATEA is that which will minimize waste discharge for those plants choosing to utilize wet air pollution control systems.

Category II

Although the possibility remains of developing baghouses which are explosion-proof and thus applicable to covered furnaces, it is by no means clear that this is a practical alternative. There is one such baghouse on a covered furnace in the world, but none in the United States. One other furnace utilizes a "candle filter" (ceramic filter) for dry cleaning of CO gas. At this time, and with only two closed furnaces in the world so equipped, it does not seem practical to require the use of a dry dust collection system. Therefore, the treatment level specified for BATEA, Category II appears to be that which will minimize waste discharge.

Category III

Some plants may be able to achieve no discharge of pollutants from slag processing operations by discharging blowdown into closed lagoons, where the blowdown will be evaporated. However, due to varying soil characteristics, other plants, if attempting to use such techniques, would have leaching to ground water. Sealed lagoons may not be practicable for all plants, and additionally, may require large land areas. Therefore, the BATEA treatment is selected as the basis for limitations from new sources.

SUMMARY

The effluent lcads, together with estimated costs, applicable to the New Source Performance Standards are summarized in Table 101.

the new source performance standards, it should be additionally For specified that all measurements taken for purposes of meeting the should be at the plant outfall, if the new source is a effluent limits new plant. This means, in effect, that run-off from materials handling storage, slag piles, collected air borne particulates, and general and plant areas must be collected and treated or that storm water must not initially contact such sources of pollutants. Such control measures can rather easily be built into new plants, but would be very difficult to accomplish in clder plants, having many years of accumulation of slag, collected airborne particulates, etc. Practical control measures might include impoundment of storm water and use of such water as an intake source or landfill of waste particulates. The option of treating runoff to meet the effluent standard would, of course, be available. The standards should be applied by the "building block" approach, These as discussed in section IX. If the hypothetical plant of that section were new source, the permissible suspended solids discharge would be 97 lb/day (44 kg/day).

PRETREATMENT STANDARDS

The raw wastes from the three categories included in this document are all generally high in metals (manganese and chromium (total and hexavalent)), as well as suspended solids. The wastes from Category II additionally contain cyanide and phenols. The metals are of particular concern, if the wastes are discharged directly to publicly owned treatment systems, since they tend to pass through such treatment works, essentially untreated or removed. The other parameters are of less concern, since (in the concentrations found in the typical raw waste in this industry), they will be treated or removed by the municipal system, and should, for this industry, be classified as "compatible pollutants." however, fall under the general classification of The metals, "incompatible pollutants," and therefore, a determination has been made that the wastes from these three categories should be treated to the level of best practicable technology (for existing sources) and to the level of the new source performance standards (for new sources).

The pretreatment standards under section 307(c) of the Act, for a source within the ferrcalloy industry which is an industrial user of a publicly owned treatment works (and which would be a new source subject to section 306 of the Act, if it were to discharge to navigable waters), shall be the standard set forth in Part 128, 40 CFR, except that the pretreatment standard for incompatible pollutants shall be the standard of performance for new sources of that subcategory. If the publicly owned treatment works 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.

			GORY I				GORY II*		CATEGORY III				
	_30 Day	Average	_24 hr M	laximum	30 Day Average 24 hr Maximum			30 Day Av kg/kkg	verage 1b/ton	24 hr Maximum kg/kkg lb/ton			
	kg/mwhr	1b/mwhr	kg/mwhr	lb/mwhr	kg/mwhr	1b/mwhr	kg/mwhr	1b/mwhr		processed	processed	processe	
Suspended Solids Total Chromium Hexavalent	.012 .0004	.026 .0009	.024 .0008	.052 .0017	.016 .0005	.035 .0012	.032 .001	.071 .002	.136 .0027	.271 .0054	.271 .0054	.542 .011	
Chromium Total Cyanide	.00004	.0001	.00008	.0002	.00005	.0001 .0006	.0001	.0002			ar <i>i</i>		
Manganese Phenol pH	.0039	.0086 6.0-9	•008	.017	.005 .0002	.012 .0005 6.0-9	.011 .0004	.023 .0009	.027	.054 6.0-	.054	.108	
F						010							
Cost Item	<u>\$/mw</u>	\$/mwh	r		\$/mw	\$/mwhr			<pre>\$/ton/yr</pre>	\$/to	n		
Investment	21,063				27,303				2,604		_		
Capital Costs Depreciation Operating Costs		0.127 0.169				0.165 0.219				0.35 0.48			
Less Power		0,745				0.965				0.42			
Power Costs Total Operating		0.015				0.019				0.05	1		
Costs		1.056				1.368				1.31			

Table 101 NEW SOURCE PERFORMANCE STANDARDS

*For non-electric furnace smelting operations, read units as kg/kkg (1b/ton), rather than kg/mwhr (1b/mwhr) and multiply the metric unit limitations by 3.3 and the English unit limitations by 3.0.

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SECTION XII

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SECTION XIV

GLOSSARY

Blocking chrome - A high 10-12 percent silicon grade of high carbon (HC) Ferrochromium, used as an additive in the making of chromium steel where it 'blocks' (i.e., stops) the reaction in the ladle.

Charge Chrome - A grade of HC ferrochromium, so called because it forms part of the charge in the making of stainless steel.

<u>Charging</u> - The process by which raw materials ("charge") are added to the furnace.

<u>Chrome ore - lime melt</u> A melt of chromium ore and lime produced in an open arc furnace and an intermediate in the production of low carbon (LC) ferrochromium.

<u>Covered furnace</u> - 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).

<u>Exothermic Process</u> - Silicon or aluminum, or a combination of the two, combine with oxygen of the charge, generating considerable heat and creating temperatures of several thousand degrees in the reaction vessel. The process is generally used to produce high grade alloys with low carbon content.

<u>Ferroalloy</u> - 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.

<u>Induction furnace</u> - Induction heating is obtained by inducing an electric current in the charge and may be considered as operating on the transformer principle. Induction furnaces, which may be low frequency or high frequency, are used to produce small tonnages of specialty alloys through remelting of the required constituents.

<u>Open furnace</u> - 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.

<u>Open arc furnace</u> - Heat is generated in an open arc furnace by the passage of an electric arc, either between two electrodes or between one or more electrodes and the charge. The arc furnace consists of a furnace chamber and two or more electrodes. The furnace chamber has a lining which can withstand the operating temperatures and which is suitable for the material to be heated. The lining is contained within a steel shell which, in most cases, can be tilted or moved.

<u>Pre-baked electrodes</u> - An electrode purchased in finished form available in diameters up to about 130 cm (51 in.). These electrodes come in sections with threaded ends, and are added to the electrode column.

<u>Reducing Agent</u> - Carbon bearing materials, such as metallurigical 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.

<u>Sintering</u> - 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, cr otherwise bind together. This may occur in the furnace itself, in which case the charge must be stoked to break up the agglomeration.

Steam/hot water scrubber - A system for removing particulates from furnace gases, where water is first heated by the gases to partially form steam, and then intimately contacted with the dirty gases. The scrubber water containing the particulates is then separated from the cleaned gases, which are emitted to the atmosphere. This system is characterized by a low water usage and pressure drop.

<u>Stoking</u> - The stirring up of the upper portion of the charged materials in the furnace. This loosens the charge and allows free upward flow of furnace gases.

<u>Submerged-arc furnace</u> - 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 almost entirely of the resistant type.

<u>Tapping</u> - 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.

Vacuum furnace - A furnace in which the charge can be brought to an elevated temperature in a high vacuum. The high vacuum provides an almost completely inert enclosure where the process of reduction and sintering can occur.