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AIR POLLUTANT EMISSION FACTORS

APTD-0922

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TRW
SYSTEMS GROUP OF TRW INC.

FERROALLOY PRODUCTION

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

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

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

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

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

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

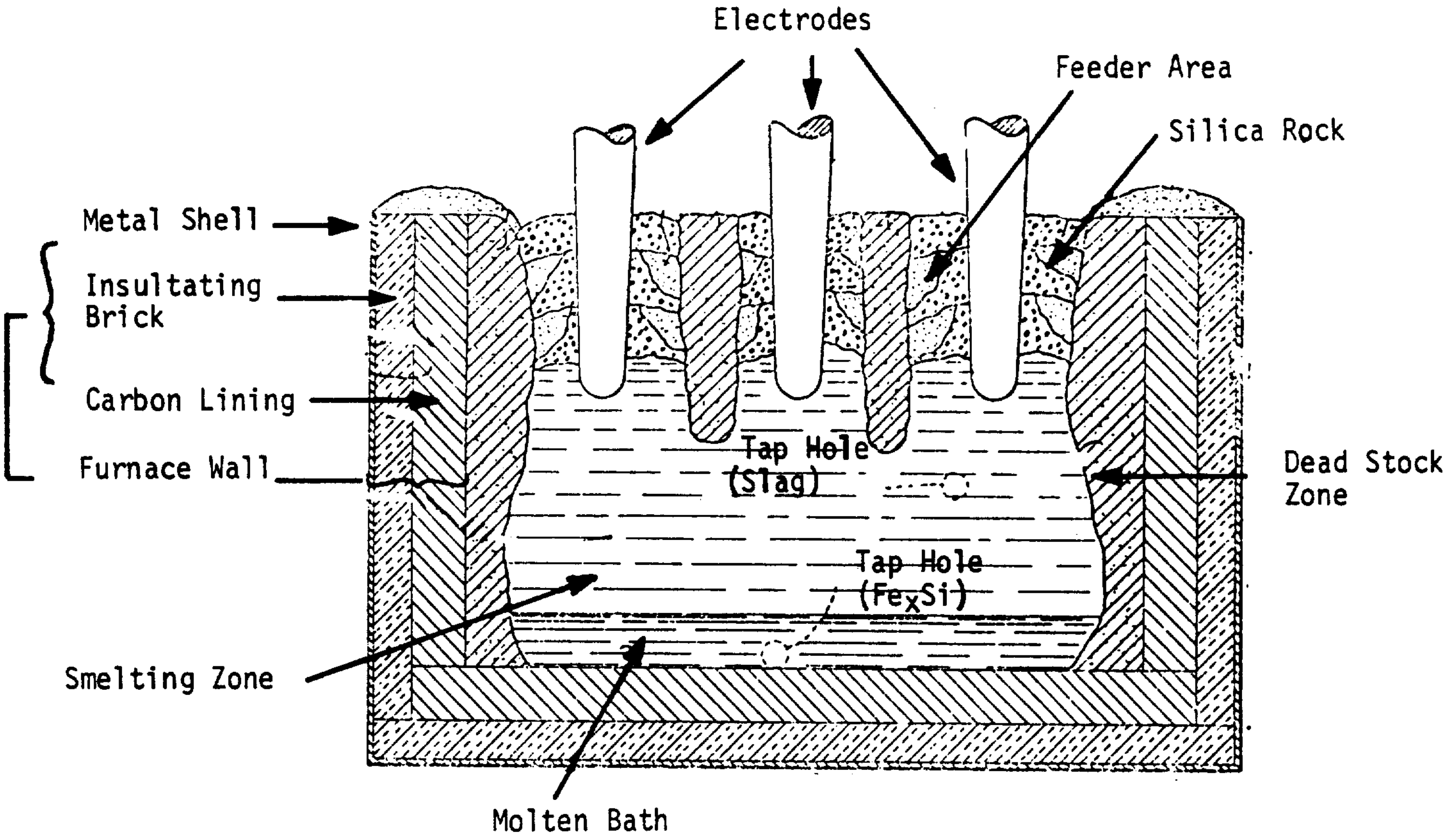

Figure 9.[17] Vertical Section of a Ferrosilicon Producing Electric Furnace

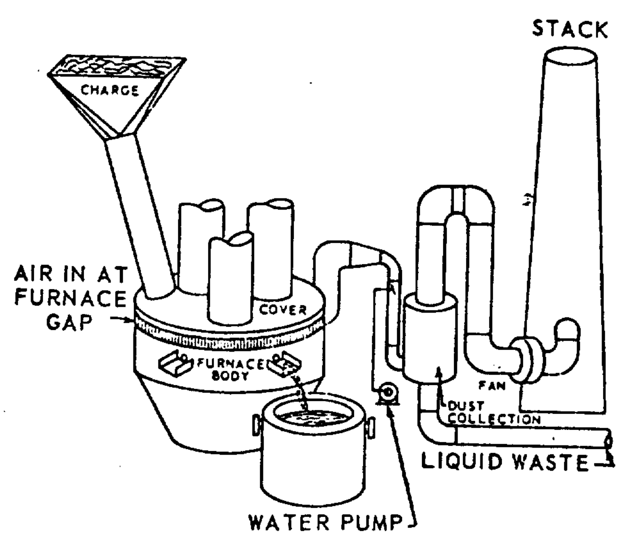

Figure 10. Electric Furnace for Ferroalloys Industry

EMISSION SOURCES

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

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

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

Table VIII. Percentage of Production for Primary Ferroalloys

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

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

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

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

FACTORS AFFECTING EMISSIONS

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

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

FERROSILICON

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

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

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

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

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

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

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

FERROMANGANESE

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

- Alloys with a low manganese content

  5 - 20 percent manganese
  3 1/2 - 5 percent carbon

  15 - 20 percent manganese
  10 percent silicon
  5 percent carbon

- Alloys with a high carbon content

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

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

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

FERROCHROMIUM, SILICOMANGANESE, FERROSILICOCHROME

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

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

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

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

EMISSION FACTORS

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

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

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

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

APPENDIX

Particulate Emission Data - Ferroalloys Production Emission Factor

Pounds of Fume/Ton of Specified Product		Reference
130	50% FeSi	18
208	50% FeSi	18
260	50% FeSi	18
200-400	75% FeSi	19
315	75% FeSi	17
500	90% FeSi	18
585	90% FeSi	18
605	90% FeSi	18
470-520	Silicon Metal	20
600-700	Silicon Metal	18
22-65	FeMn	19
200	SiMn	19
190	SiMn	19

Computation on Emission of CO Based on 2 Mols of CO Per Mol of Ferroalloy

Atomic Weights

Fe:	56	Si:	28	C:	12
		Mn:	55	O:	16
		Cr:	52		

Unit Weight of CO = 2(28) = 56g

Unit Weight of Ferroalloy: from $\frac{2}{n+1}$ (Fe + nSi)

50% FeSi = $\frac{2}{2}$(Fe + Si) = 84g

75% FeSi = $\frac{2}{4}$(Fe + 3Si) = 70g

90% FeSi = $\frac{2}{10}$(Fe + 9Si) = 61.6g

FeMn = 111

FeCr = 108

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

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

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

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

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

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

Reliability of Emission Factors

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

Table IXa. Ranking of Emission Factors

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

REFERENCES

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19. Fredriksen and Nestaas. "Pollution Problems by Electric Furnace Ferroalloy Production." United Nations Economic Commission for Europe. September 1968.

20. Gerstle and McGinnity. Plant Visit Memorandum. U.S. Department of Health, Education and Welfare. Public Health Service. June 1967.