

ESR (ELECTRO SLAG REFINING)

- ESR has been known since the 1930s, but it took approx 30 years before it became an acknowledged process for mass production of high-quality ingots. The ESR technology is of interest not only for the production of smaller weight ingots of tool steels and super alloys, but also of heavy forging ingots up to raw ingot weights of 165 tons.

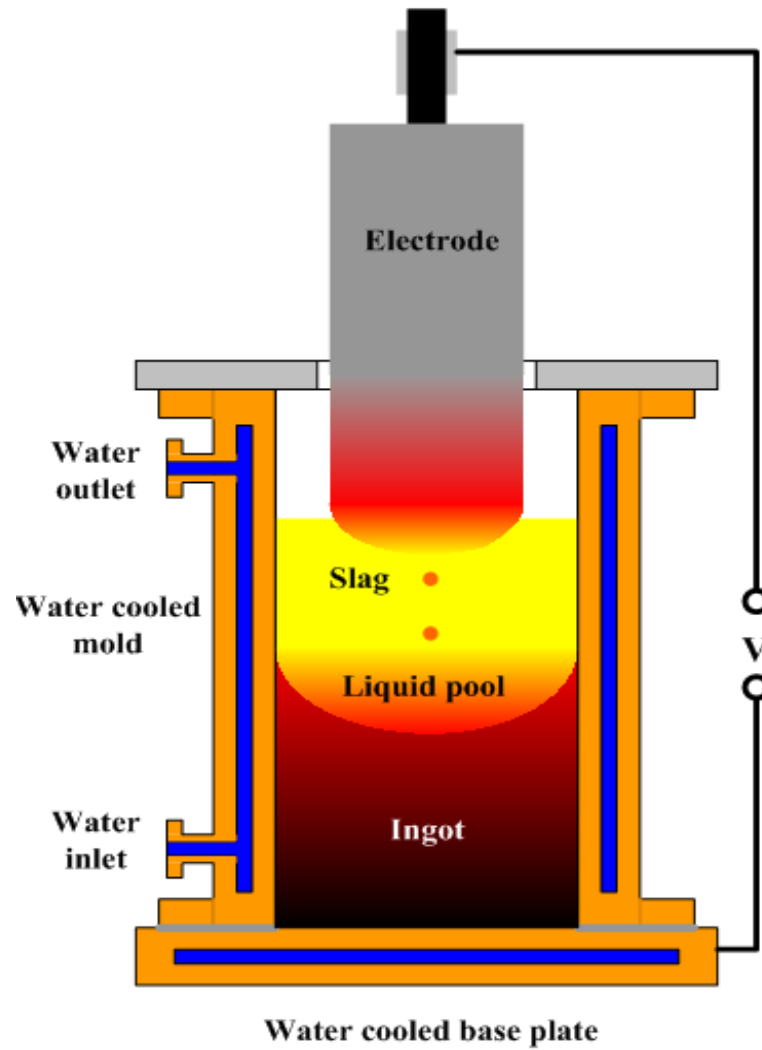
- It is a process of remelting and refining steel and other alloys for mission-critical applications in aircraft, thermal power stations, nuclear power plants, military technology.

- The consumable electrodes are as cast or forged cylindrical parts made of an alloy to be remelt.
- An electroslag remelting process (ESR) starts when the lower tip of a consumable electrode is immersed into a pool of molten slag.
- The premelted slag possessing electrical conductivity is located on the water-cooled mold base connected to a power supply.
- The electric current (commonly AC) passing through the the slag keeps it at high temperature, which is about (200°C) higher than the melting point of the remelted metal.

- The electrode tip is heated by the hot slag and starts to melt forming droplets of liquid metal, which disconnect from the electrode and sink through the slag layer.
- The slag composition is based on calcium fluoride (CaF_2), lime (CaO) and alumina (A
- The molten steel in form of both liquid film on the electrode tip and descending droplets contacts with the slag and get refined due to desulfurization and removal of non-metallic inclusions (Sulfides and Oxides). l_2O_3).

- The droplets enter the molten steel pool, bottom of which is progressively solidifying. The water-cooled copper mold provides relatively high gradient of temperature resulting in high solidification rate. Solidification front is moving upwards (unidirectional solidification) forming sound homogeneous metal structure.
- The ingot has a good surface quality due to a thin slag film covering it.

Electroslag remelting



THE SLAG COMPOSITION PROVIDES THE FOLLOWING PROPERTIES:

- Melting point lower than that of the remelted alloy.
- Required level of viscosity.
- Required level of electrical conductivity.
- High solubility of sulfur.
- Capability to adsorb non-metallic inclusions.

METALLURGY OF THE ESR

Slags for ESR are usually based on calcium fluoride (CaF_2), lime (CaO) and alumina (Al_2O_3). Magnesia (MgO), titania (TiO_2) and silica (SiO_2) may also be added, depending on the alloy

to be remelted. To perform its intended functions, the slag must

have some well-defined properties, such as:

- Its melting point must be lower than that of the metal to be remelted;
- It must be electrically efficient;
- Its composition should be selected to ensure the desired chemical reactions;
- It must have suitable viscosity at remelting temperature.

INERT GAS MELTING

A new trend is emerging in ESR melting that involves melting of Oxygen and Nitrogen sensitive alloys under an inert gas enclosure. The major benefits of the inert gas melting system, besides very low oxygen and nitrogen levels, are as follows:

- The system is fully enclosed preventing the possibility of contamination from the melt shop during melting.
- Different slags can be used because the oxidation of the slag is no longer a concern
- No deoxidant is required. Deoxidant has been shown to be a principal source of inclusions in ESR ingots.

ADVANTAGES

- Deep desulfurization.
- Refining non-metallic inclusions.
- Homogeneous distribution of non-metallic inclusions.
- Fine Grain structure.
- No Shrinkage defects.
- Low macrosegregation.
- Good surface quality.
- Controllable process.

APPLICATIONS

- Tool steels for milling cutters, mining, etc.
- Die steels for the glass, plastics and automotive industries.
- Ball-bearing steels.
- Steels for turbine and generator shafts.
- Superalloys for aerospace and power turbines.
- Nickel-base alloys for the chemical industry.
- Cold rolls.

12.4 Ferroalloy Production

12.4.1 General

Ferroalloy is an alloy of iron with some element other than carbon. Ferroalloy is used to physically introduce or "carry" that element into molten metal, usually during steel manufacture. In practice, the term ferroalloy is used to include any alloys that introduce reactive elements or alloy systems, such as nickel and cobalt-based aluminum systems. Silicon metal is consumed in the aluminum industry as an alloying agent and in the chemical industry as a raw material in silicon-based chemical manufacturing.

The ferroalloy industry is associated with the iron and steel industries, its largest customers. Ferroalloys impart distinctive qualities to steel and cast iron and serve important functions during iron and steel production cycles. The principal ferroalloys are those of chromium, manganese, and silicon. Chromium provides corrosion resistance to stainless steels. Manganese is essential to counteract the harmful effects of sulfur in the production of virtually all steels and cast iron. Silicon is used primarily for deoxidation in steel and as an alloying agent in cast iron. Boron, cobalt, columbium, copper, molybdenum, nickel, phosphorus, titanium, tungsten, vanadium, zirconium, and the rare earths impart specific characteristics and are usually added as ferroalloys.

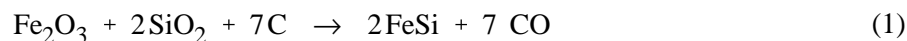
United States ferroalloy production in 1989 was approximately 894,000 megagrams (Mg) (985,000 tons), substantially less than shipments in 1975 of approximately 1,603,000 megagrams (1,770,000 tons). In 1989, ferroalloys were produced in the U. S. by 28 companies, although 5 of those produced only ferrophosphorous as a byproduct of elemental phosphorous production.

12.4.2 Process Description

A typical ferroalloy plant is illustrated in Figure 12.4-1. A variety of furnace types, including submerged electric arc furnaces, exothermic (metallothermic) reaction furnaces, and electrolytic cells can be used to produce ferroalloys. Furnace descriptions and their ferroalloy products are given in Table 12.4-1.

12.4.2.1 Submerged Electric Arc Process -

In most cases, the submerged electric arc furnace produces the desired product directly. It may produce an intermediate product that is subsequently used in additional processing methods. The submerged arc process is a reduction smelting operation. The reactants consist of metallic ores (ferrous oxides, silicon oxides, manganese oxides, chrome oxides, etc.) and a carbon-source reducing agent, usually in the form of coke, charcoal, high- and low-volatility coal, or wood chips. Limestone may also be added as a flux material. Raw materials are crushed, sized, and, in some cases, dried, and then conveyed to a mix house for weighing and blending. Conveyors, buckets, skip hoists, or cars transport the processed material to hoppers above the furnace. The mix is then gravity-fed through a feed chute either continuously or intermittently, as needed. At high temperatures in the reaction zone, the carbon source reacts with metal oxides to form carbon monoxide and to reduce the ores to base metal. A typical reaction producing ferrosilicon is shown below:



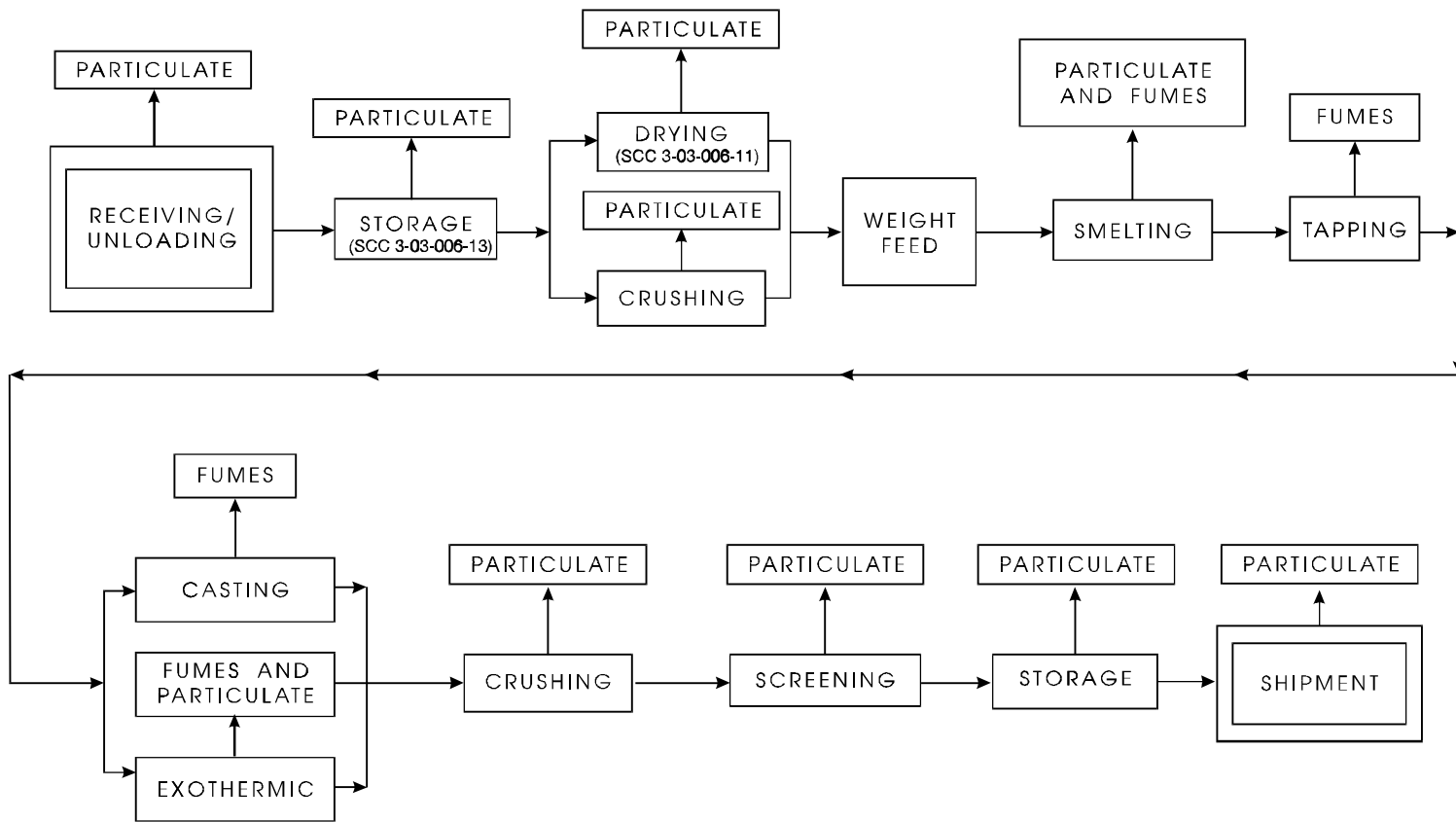


Figure 12.4-1. Typical ferroalloy production process. (Source Classification Code in parentheses.)

Table 12.4-1. FERROALLOY PROCESSES AND RESPECTIVE PRODUCT GROUPS

| Process | Product |
|--|--|
| Submerged arc furnace ^a | Silvery iron (15-22% Si) Ferrosilicon (50% Si) Ferrosilicon (65-75% Si) Silicon metal Silicon/manganese/zirconium (SMZ) High carbon (HC) ferromanganese Siliconmanganese HC ferrochrome Ferrochrome/silicon FeSi (90% Si) |
| Exothermic ^b Silicon reduction | Low carbon (LC) ferrochrome, LC ferromanganese, medium carbon (MC) ferromanganese |
| Aluminum Reduction | Chromium metal, ferrotitanium, ferrocolumbium, ferovanadium |
| Mixed aluminothermal/silicothermal | Ferromolybdenum, ferrotungsten |
| Electrolytic ^c | Chromium metal, manganese metal |
| Vacuum furnace ^d | LC ferrochrome |
| Induction furnace ^e | Ferrotitanium |

^a Process by which metal is smelted in a refractory-lined cup-shaped steel shell by submerged graphite electrodes.

^b Process by which molten charge material is reduced, in exothermic reaction, by addition of silicon, aluminum, or a combination of the 2.

^c Process by which simple ions of a metal, usually chromium or manganese in an electrolyte, are plated on cathodes by direct low-voltage current.

^d Process by which carbon is removed from solid-state high-carbon ferrochrome within vacuum furnaces maintained at temperatures near melting point of alloy.

^e Process that converts electrical energy into heat, without electrodes, to melt metal charges in a cup or drum-shaped vessel.

Smelting in an electric arc furnace is accomplished by conversion of electrical energy to heat. An alternating current applied to the electrodes causes current to flow through the charge between the electrode tips. This provides a reaction zone at temperatures up to 2000°C (3632°F). The tip of each electrode changes polarity continuously as the alternating current flows between the tips. To maintain a uniform electric load, electrode depth is continuously varied automatically by mechanical or hydraulic means.

A typical submerged electric arc furnace design is depicted in Figure 12.4-2. The lower part of the submerged electric arc furnace is composed of a cylindrical steel shell with a flat bottom or hearth. The interior of the shell is lined with 2 or more layers of carbon blocks. The furnace shell may be water-cooled to protect it from the heat of the process. A water-cooled cover and fume collection hood are mounted over the furnace shell. Normally, 3 carbon electrodes arranged in a triangular formation extend through the cover and into the furnace shell opening. Prebaked or self-baking (Soderberg) electrodes ranging from 76 to over 100 cm (30 to over 40 inches) in diameter are typically used. Raw materials are sometimes charged to the furnace through feed chutes from above the furnace. The surface of the furnace charge, which contains both molten material and unconverted charge during operation, is typically maintained near the top of the furnace shell. The lower ends of the electrodes are maintained at about 0.9 to 1.5 meters (3 to 5 feet) below the charge surface. Three-phase electric current arcs from electrode to electrode, passing through the charge material. The charge material melts and reacts to form the desired product as the electric energy is converted into heat. The carbonaceous material in the furnace charge reacts with oxygen in the metal oxides of the charge and reduces them to base metals. The reactions produce large quantities of carbon monoxide (CO) that passes upward through the furnace charge. The molten metal and slag are removed (tapped) through 1 or more tap holes extending through the furnace shell at the hearth level. Feed materials may be charged continuously or intermittently. Power is applied continuously. Tapping can be intermittent or continuous based on production rate of the furnace.

Submerged electric arc furnaces are of 2 basic types, open and covered. Most of the submerged electric arc furnaces in the U. S. are open furnaces. Open furnaces have a fume collection hood at least 1 meter (3.3 feet) above the top of the furnace shell. Moveable panels or screens are sometimes used to reduce the open area between the furnace and hood, and to improve emissions capture efficiency. Carbon monoxide rising through the furnace charge burns in the area between the charge surface and the capture hood. This substantially increases the volume of gas the containment system must handle. Additionally, the vigorous open combustion process entrains finer material in the charge. Fabric filters are typically used to control emissions from open furnaces.

Covered furnaces may have a water-cooled steel cover that fits closely to the furnace shell. The objective of covered furnaces is to reduce air infiltration into the furnace gases, which reduces combustion of that gas. This reduces the volume of gas requiring collection and treatment. The cover has holes for the charge and electrodes to pass through. Covered furnaces that partially close these hood openings with charge material are referred to as "mix-sealed" or "semi-enclosed furnaces". Although these covered furnaces significantly reduce air infiltration, some combustion still occurs under the furnace cover. Covered furnaces that have mechanical seals around the electrodes and sealing compounds around the outer edges are referred to as "sealed" or "totally closed". These furnaces have little, if any, air infiltration and undercover combustion. Water leaks from the cover into the furnace must be minimized as this leads to excessive gas production and unstable furnace operation. Products prone to highly variable releases of process gases are typically not made in covered furnaces for safety reasons. As the degree of enclosure increases, less gas is produced for capture by the hood system and the concentration of carbon monoxide in the furnace gas increases. Wet scrubbers are used to control emissions from covered furnaces. The scrubbed, high carbon monoxide content gas may be used within the plant or flared.

The molten alloy and slag that accumulate on the furnace hearth are removed at 1 to 5-hour intervals through the tap hole. Tapping typically lasts 10 to 15 minutes. Tap holes are opened with pellet shot from a gun, by drilling, or by oxygen lancing. The molten metal and slag flow from the tap hole into a carbon-lined trough, then into a carbon-lined runner that directs the metal and slag into a reaction ladle, ingot molds, or chills. (Chills are low, flat iron or steel pans that provide rapid

CARBON ELECTRODES

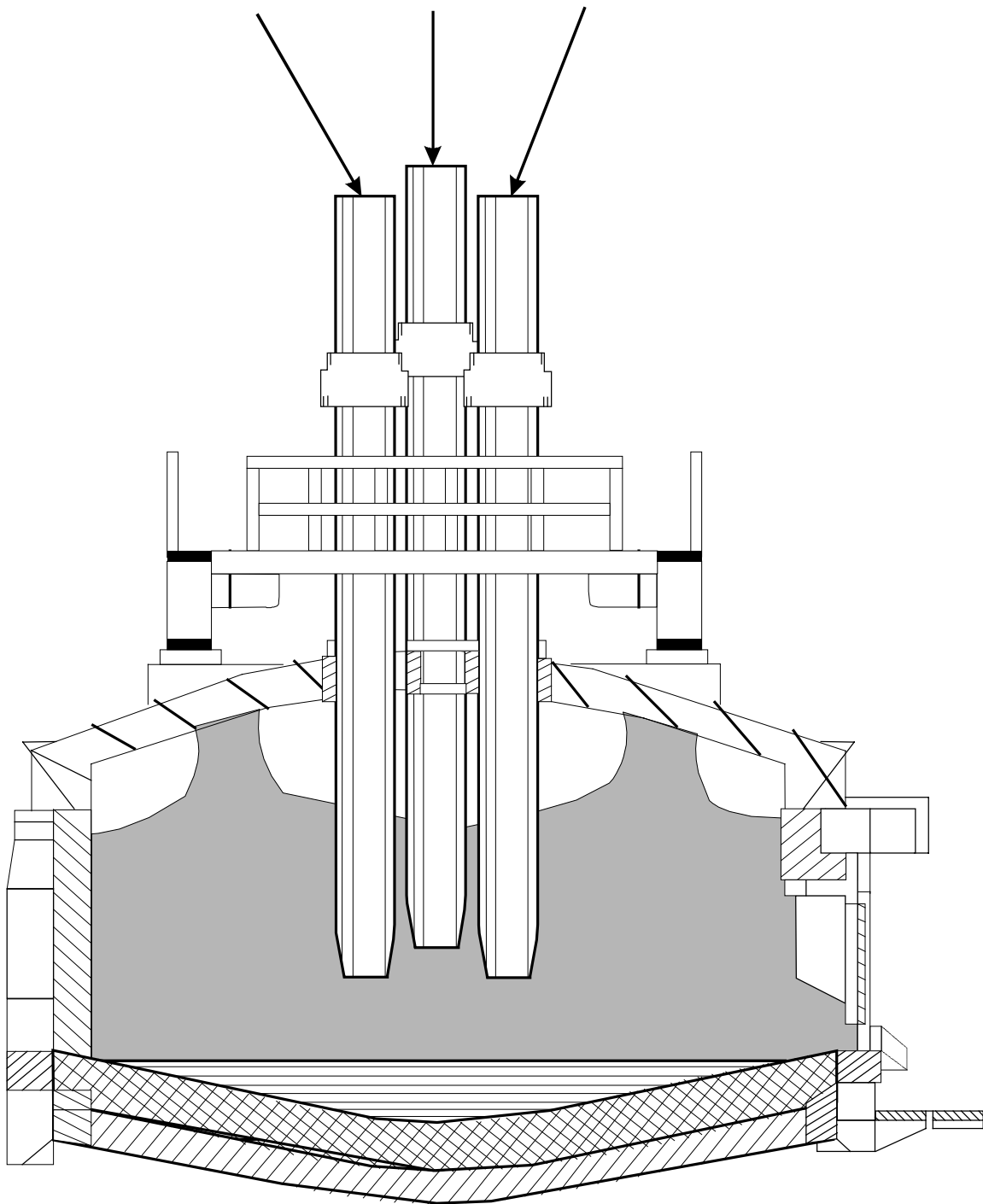


Figure 12.4-2. Typical submerged arc furnace design.

cooling of the molten metal.) After tapping is completed, the furnace is resealed by inserting a carbon paste plug into the tap hole.

Chemistry adjustments may be necessary after furnace smelting to achieve a specified product. Ladle treatment reactions are batch processes and may include metal and alloy additions.

During tapping, and/or in the reaction ladle, slag is skimmed from the surface of the molten metal. It can be disposed of in landfills, sold as road ballast, or used as a raw material in a furnace or reaction ladle to produce a chemically related ferroalloy product.

After cooling and solidifying, the large ferroalloy castings may be broken with drop weights or hammers. The broken ferroalloy pieces are then crushed, screened (sized), and stored in bins until shipment. In some instances, the alloys are stored in lump form in inventories prior to sizing for shipping.

12.4.2.2 Exothermic (Metallothermic) Process -

The exothermic process is generally used to produce high-grade alloys with low-carbon content. The intermediate molten alloy used in the process may come directly from a submerged electric arc furnace or from another type of heating device. Silicon or aluminum combines with oxygen in the molten alloy, resulting in a sharp temperature rise and strong agitation of the molten bath. Low- and medium-carbon content ferrochromium (FeCr) and ferromanganese (FeMn) are produced by silicon reduction. Aluminum reduction is used to produce chromium metal, ferrotitanium, ferrovandium, and ferrocolumbium. Mixed aluminosilico thermal processing is used for producing ferromolybdenum and ferrotungsten. Although aluminum is more expensive than carbon or silicon, the products are purer. Low-carbon (LC) ferrochromium is typically produced by fusing chromium ore and lime in a furnace. A specified amount is then placed in a ladle (ladle No. 1). A known amount of an intermediate grade ferrochromesilicon is then added to the ladle. The reaction is extremely exothermic and liberates chromium from its ore, producing LC ferrochromium and a calcium silicate slag. This slag, which still contains recoverable chromium oxide, is reacted in a second ladle (ladle No. 2) with molten high-carbon ferrochromesilicon to produce the intermediate-grade ferrochromesilicon. Exothermic processes are generally carried out in open vessels and may have emissions similar to the submerged arc process for short periods while the reduction is occurring.

12.4.2.3 Electrolytic Processes -

Electrolytic processes are used to produce high-purity manganese and chromium. As of 1989, there were 2 ferroalloy facilities using electrolytic processes.

Manganese may be produced by the electrolysis of an electrolyte extracted from manganese ore or manganese-bearing ferroalloy slag. Manganese ores contain close to 50 percent manganese; furnace slag normally contains about 10 percent manganese. The process has 5 steps: (1) roasting the ore to convert it to manganese oxide (MnO), (2) leaching the roasted ore with sulfuric acid (H₂SO₄) to solubilize manganese, (3) neutralization and filtration to remove iron and aluminum hydroxides, (4) purifying the leach liquor by treatment with sulfide and filtration to remove a wide variety of metals, and (5) electrolysis.

Electrolytic chromium is generally produced from high-carbon ferrochromium. A large volume of hydrogen gas is produced by dissolving the alloy in sulfuric acid. The leachate is treated with ammonium sulfate and conditioned to remove ferrous ammonium sulfate and produce a chrome-alum for feed to the electrolysis cells. The electrolysis cells are well ventilated to reduce ambient hydrogen and hexavalent chromium concentrations in the cell rooms.

12.4.3 Emissions And Controls

Particulate is generated from several activities during ferroalloy production, including raw material handling, smelting, tapping, and product handling. Organic materials are generated almost exclusively from the smelting operation. The furnaces are the largest potential sources of particulate and organic emissions. The emission factors are given in Tables 12.4-2 and 12.4-3. Size-specific emission factors for submerged arc ferroalloy furnaces are given in Tables 12.4-4 and 12.4-5.

Particulate emissions from electric arc furnaces in the form of fumes account for an estimated 94 percent of the total particulate emissions in the ferroalloy industry. Large amounts of carbon monoxide and organic materials also are emitted by submerged electric arc furnaces. Carbon monoxide is formed as a byproduct of the chemical reaction between oxygen in the metal oxides of the charge and carbon contained in the reducing agent (coke, coal, etc.). Reduction gases containing organic compounds and carbon monoxide continuously rise from the high-temperature reaction zone, entraining fine particles and fume precursors. The mass weight of carbon monoxide produced sometimes exceeds that of the metallic product. The heat-induced fume consists of oxides of the products being produced and carbon from the reducing agent. The fume is enriched by silicon dioxide, calcium oxide, and magnesium oxide, if present in the charge.

In an open electric arc furnace, virtually all carbon monoxide and much of the organic matter burns with induced air at the furnace top. The remaining fume, captured by hooding about 1 meter above the furnace, is directed to a gas cleaning device. Fabric filters are used to control emissions from 85 percent of the open furnaces in the U. S. Scrubbers are used on 13 percent of the furnaces, and electrostatic precipitators on 2 percent.

Two emission capture systems, not usually connected to the same gas cleaning device, are necessary for covered furnaces. A primary capture system withdraws gases from beneath the furnace cover. A secondary system captures fumes released around the electrode seals and during tapping. Scrubbers are used almost exclusively to control exhaust gases from sealed furnaces. The scrubbers capture a substantial percentage of the organic emissions, which are much greater for covered furnaces than open furnaces. The gas from sealed and mix-sealed furnaces is usually flared at the exhaust of the scrubber. The carbon monoxide-rich gas is sometimes used as a fuel in kilns and sintering machines. The efficiency of flares for the control of carbon monoxide and the reduction of VOCs has been estimated to be greater than 98 percent. A gas heating reduction of organic and carbon monoxide emissions is 98 percent efficient.

Tapping operations also generate fumes. Tapping is intermittent and is usually conducted during 10 to 20 percent of the furnace operating time. Some fumes originate from the carbon lip liner, but most are a result of induced heat transfer from the molten metal or slag as it contacts the runners, ladles, casting beds, and ambient air. Some plants capture these emissions to varying degrees with a main canopy hood. Other plants employ separate tapping hoods ducted to either the furnace emission control device or a separate control device. Emission factors for tapping emissions are unavailable due to lack of data.

After furnace tapping is completed, a reaction ladle may be used to adjust the metallurgy by chlorination, oxidation, gas mixing, and slag metal reactions. Ladle reactions are an intermittent process, and emissions have not been quantified. Reaction ladle emissions are often captured by the tapping emissions control system.

Table 12.4-2 (Metric Units). EMISSION FACTORS FOR PARTICULATE FROM SUBMERGED ARC FERROALLOY FURNACES^a

| Product ^b | Furnace Type | Particulate Emission Factors Uncontrolled ^c | EMISSION FACTOR RATING | Control Device ^d | Particulate Emission Factors Controlled ^c | EMISSION FACTOR RATING |
|--------------------------------------|------------------------|--|------------------------|------------------------------|--|------------------------|
| FeSi (50%) (SCC 3-03-006-01) | Open ^{e,f,g} | 35 | B | Baghouse ^{e,f} | 0.9 | B |
| | Covered ^h | 46 | E | Scrubber ^{h,j} | | |
| High energy | | | | 0.24 | E | |
| FeSi (75%) (SCC 3-03-006-02) | Open ^k | 158 | E | Scrubber ^{h,j} | | |
| | | | | Low energy | 4.5 | E |
| FeSi (90%) (SCC 3-03-006-03) | Open ^m | 282 | E | ND | ND | NA |
| | | | | Covered ^{h,j} | 103 | E |
| Si metal (98%) (SCC 3-03-006-04) | Open ^{n,p} | 436 | B | Baghouse ^{n,p} | 16 | B |
| FeMn (80%) (SCC 3-03-006-06) | Open ^{q,r} | 14 | B | Baghouse ^{q,r} | 0.24 | B |
| | | | | Scrubber ^{h,s} | | |
| FeMn (1% Si) (SCC 3-03-007-01) | Covered ^{h,t} | 6 | E | High energy | 0.8 | E |
| | | | | Scrubber | 0.25 | C |
| FeCr (high carbon) (SCC 3-03-006-07) | Sealed ^{u,v} | 37 | E | High energy ^{h,s,w} | | |
| | | | | ND | ND | NA |
| SiMn (SCC 3-03-006-05) | Open ^{x,y} | 78 | C | ESP ^{x,y} | 1.2 | C |
| | | | | Open ^{z,aa} | 96 | C |
| | Sealed | — | — | Scrubber ^{v,w} | | |
| | | | | High energy | 0.15 | C |

^a Emission factors are expressed as kg of pollutant/Mg alloy produced. Factors are for main furnace dust collection system before and after control device. Where other emissions, such as leaks or tapping, are included or quantified separately, such is noted. Particulate sources not included: raw material handling, storage, and preparation; and product crushing, screening, handling, and packaging. SCC = Source Classification Code. ND = no data. NA = not applicable.

^b Percentages are of the main alloying agent in product.

Table 12.4-2 (cont.).

- ^c In most source testing, fugitive emissions are not measured or collected. Where tapping emissions are controlled by primary system, their contribution to total emissions could not be determined. Fugitive emissions may vary greatly among sources, with furnace and collection system design and operating practices.
- ^d Low-energy scrubbers are those with $\Delta P < 20$ inches of H_2O ; high-energy with $\Delta P > 20$ inches of H_2O .
- ^e Includes fumes captured by tapping hood (efficiency estimated at near 100%).
- ^f References 4,10,21.
- ^g Factor is average of 3 sources, fugitive emissions not included. Fugitive emissions at 1 source measured an additional 10.5 kg/Mg alloy, or 2.7 kg/MW-hr.
- ^h References 4,10.
- ^j Does not include emissions from tapping or mix seal leaks.
- ^k References 25-26.
- ^m Reference 23.
- ⁿ Estimated 60% of tapping emissions captured by control system (escaped fugitive emissions not included in factor).
- ^p References 10,13.
- ^q Estimated 50% of tapping emissions captured by control system (escaped fugitive emissions not included in factor).
- ^r References 4,10,12.
- ^s Includes fumes only from primary control system.
- ^t Includes tapping fumes and mix seal leak fugitive emissions. Fugitive emissions measured at 33% of total uncontrollable emissions.
- ^u Assumes tapping fumes not included in emission factor.
- ^v Reference 14.
- ^w Does not include tapping or fugitive emissions.
- ^x Tapping emissions included.
- ^y References 2,15-17.
- ^z Factor is average of 2 test series. Tests at 1 source included fugitive emissions (3.4% of total uncontrolled emissions). Second test insufficient to determine if fugitive emissions were included in total.
- ^{aa} References 2,18-19.
- ^{bb} Factors developed from 2 scrubber controlled sources, 1 operated at $\Delta P = 47-57$ inches of H_2O , the other at unspecified ΔP . Uncontrolled tapping operations emissions are 2.1 kg/Mg alloy.

Table 12.4-3 (English Units). EMISSION FACTORS FOR PARTICULATE FROM SUBMERGED ARC FERROALLOY FURNACES^a

| Product ^b | Furnace Type | Particulate Emission factors Uncontrolled ^c | EMISSION FACTOR RATING | Control Device ^d | Particulate Emission factors Controlled ^c | EMISSION FACTOR RATING |
|--------------------------------------|------------------------|--|------------------------|------------------------------|--|------------------------|
| FeSi (50%) (SCC 3-03-006-01) | Open ^{e,f,g} | 70 | B | Baghouse ^{e,f} | 1.8 | B |
| | Covered ^h | 92 | E | Scrubber ^{h,j} | | |
| High energy | | | | 0.48 | E | |
| FeSi (75%) (SCC 3-03-006-02) | Open ^k | 316 | E | Scrubber ^{h,j} | | |
| | | | | Low energy | 9.0 | E |
| FeSi (90%) (SCC 3-03-006-03) | Covered ^{h,j} | 206 | E | ND | ND | NA |
| | | | | Open ^m | 564 | E |
| Si metal (98%) (SCC 3-03-006-04) | Open ^{n,p} | 872 | B | Baghouse ^{n,p} | 32 | B |
| FeMn (80%) (SCC 3-03-006-06) | Open ^{q,r} | 28 | B | Baghouse ^{q,r} | 0.48 | B |
| | | | | Scrubber ^{h,s} | | |
| FeMn (1% Si) (SCC 3-03-007-01) | Covered ^{h,t} | 12 | E | High energy ^{h,s,w} | 1.6 | E |
| | | | | Scrubber | | |
| FeCr (high carbon) (SCC 3-03-006-07) | Sealed ^{u,v} | 74 | E | High energy ^{h,s,w} | 0.5 | C |
| | | | | ND | ND | NA |
| SiMn (SCC 3-03-006-05) | Open ^{x,y} | 157 | C | ESP ^{x,y} | 2.3 | C |
| SiMn (SCC 3-03-006-05) | Open ^{z,aa} | 192 | C | Scrubber ^{aa,bb} | 4.2 | C |
| | | | | Sealed | — | — |
| | | | | Scrubber ^{v,w} | | |
| | | | | High energy | 0.30 | C |

^a Emission factors expressed as lb of pollutant/ton of Alloy produced. Factors are for main furnace dust collection system before and after control device. Where other emissions, such as leaks or tapping, are included or quantified separately, such is noted. Particulate sources not included: raw material handling, storage, and preparation; and product crushing, screening, handling, and packaging. SCC = Source Classification Code. ND = no data. NA = not applicable.

^b Percentages are of the main alloying agent in product.

Table 12.4-3 (cont.).

- ^c In most source testing, fugitive emissions are not measured or collected. Where tapping emissions are controlled by primary system, their contribution to total emissions could not be determined. Fugitive emissions may vary greatly among sources, with furnace and collection system design and operating practices.
- ^d Low-energy scrubbers are those with $\Delta P < 20$ inches of H_2O ; high-energy with $\Delta P > 20$ inches of H_2O .
- ^e Includes fumes captured by tapping hood (efficiency estimated at near 100%).
- ^f References 4,10,21.
- ^g Factor is average of 3 sources, fugitive emissions not included. Fugitive emissions at 1 source measured an additional 21 lb/ton alloy, or 5.9 lb/MW-hr.
- ^h References 4,10.
- ^j Does not include emissions from tapping or mix seal leaks.
- ^k References 25-26.
- ^m Reference 23.
- ⁿ Estimated 60% of tapping emissions captured by control system (escaped fugitive emissions not included in factor).
- ^p References 10,13.
- ^q Estimated 50% of tapping emissions captured by control system (escaped fugitive emissions not included in factor).
- ^r References 4,10,12.
- ^s Includes fumes only from primary control system.
- ^t Includes tapping fumes and mix seal leak fugitive emissions. Fugitive emissions measured at 33% of total uncontrollable emissions.
- ^u Assumes tapping fumes not included in emission factor.
- ^v Reference 14.
- ^w Does not include tapping or fugitive emissions.
- ^x Tapping emissions included.
- ^y References 2,15-17.
- ^z Factor is average of 2 test series. Tests at 1 source included fugitive emissions (3.4% of total uncontrolled emissions). Second test insufficient to determine if fugitive emissions were included in total.
- ^{aa} References 2,18-19.
- ^{bb} Factors developed from 2 scrubber controlled sources, 1 operated at $\Delta P = 47-57$ inches of H_2O , the other at unspecified ΔP . Uncontrolled tapping operations emissions are 4.2 lb/ton alloy.

Table 12.4-4 (Metric Units). SIZE-SPECIFIC EMISSION FACTORS FOR SUBMERGED ARC FERROALLOY FURNACES

| Product | Control Device | Particle Size ^a (µm) | Cumulative Mass % ≤ Stated Size | Cumulative Mass Emission Factor (kg/Mg alloy) | EMISSION FACTOR RATING |
|---|-----------------------|------------------------------------|---------------------------------------|--|------------------------------|
| 50% FeSi Open furnace (SCC 3-03-006-01) | None ^{b,c} | 0.63 | 45 | 16 | B |
| | | 1.00 | 50 | 18 | |
| | | 1.25 | 53 | 19 | |
| | | 2.50 | 57 | 20 | |
| | | 6.00 | 61 | 21 | |
| | | 10.00 | 63 | 22 | |
| | | 15.00 | 66 | 23 | |
| | | 20.00 | 69 | 24 | |
| | | — ^d | 100 | 35 | |
| | Baghouse | 0.63 | 31 | 0.28 | B |
| | | 1.00 | 39 | 0.35 | |
| | | 1.25 | 44 | 0.40 | |
| | | 2.50 | 54 | 0.49 | |
| | | 6.00 | 63 | 0.57 | |
| | | 10.00 | 72 | 0.65 | |
| | | 15.00 | 80 | 0.72 | |
| | | 20.00 | 85 | 0.77 | |
| | | — ^d | 100 | 0.90 | |
| 80% FeMn Open furnace (SCC 3-03-006-06) | None ^{e,f} | 0.63 | 30 | 4 | B |
| | | 1.00 | 46 | 7 | |
| | | 1.25 | 52 | 8 | |
| | | 2.50 | 62 | 9 | |
| | | 6.00 | 72 | 10 | |
| | | 10.00 | 86 | 12 | |
| | | 15.00 | 96 | 13 | |
| | | 20.00 | 97 | 14 | |
| | | — ^d | 100 | 14 | |
| | Baghouse ^e | 0.63 | 20 | 0.048 | B |
| | | 1.00 | 30 | 0.070 | |
| | | 1.25 | 35 | 0.085 | |
| | | 2.50 | 49 | 0.120 | |
| | | 6.00 | 67 | 0.160 | |
| | | 10.00 | 83 | 0.200 | |
| | | 15.00 | 92 | 0.220 | |
| | | 20.00 | 97 | 0.235 | |
| | | — ^d | 100 | 0.240 | |

Table 12.4-4 (cont.).

| Product | Control Device | Particle Size ^a (µm) | Cumulative Mass % ≤ Stated Size | Cumulative Mass Emission Factor (kg/Mg alloy) | EMISSION FACTOR RATING |
|--|---------------------|------------------------------------|------------------------------------|--|------------------------|
| Si Metal ^g Open furnace (SCC 3-03-006-04) | None ^h | 0.63 | 57 | 249 | B |
| | | 1.00 | 67 | 292 | |
| | | 1.25 | 70 | 305 | |
| | | 2.50 | 75 | 327 | |
| | | 6.00 | 80 | 349 | |
| | | 10.00 | 86 | 375 | |
| | | 15.00 | 91 | 397 | |
| | | 20.00 | 95 | 414 | |
| | — ^d | 100 | 436 | | |
| | Baghouse | 1.00 | 49 | 7.8 | |
| | | 1.25 | 53 | 8.5 | |
| | | 2.50 | 64 | 10.2 | |
| | | 6.00 | 76 | 12.2 | |
| | | 10.00 | 87 | 13.9 | |
| | | 15.00 | 96 | 15.4 | |
| 20.00 | | 99 | 15.8 | | |
| 100 | 16.0 | | | | |
| FeCr (HC) Open furnace (SCC 3-03-006-07) | None ^{b,j} | 0.5 | 19 | 15 | C |
| | | 1.0 | 36 | 28 | |
| | | 2.0 | 60 | 47 | |
| | | 2.5 | 63 ^k | 49 | |
| | | 4.0 | 76 | 59 | |
| | | 6.0 | 88 ^k | 67 | |
| | | 10.0 | 91 | 71 | |
| | | — ^d | 100 | 78 | |
| | ESP | 0.5 | 33 | 0.40 | C |
| | | 1.0 | 47 | 0.56 | |
| | | 2.0 | 67 | 0.80 | |
| | | 2.5 | 80 | 0.96 | |
| | | 4.0 | 86 | 1.03 | |
| | | 6.0 | 90 | 1.08 | |
| 10.0 | 100 | 1.2 | | | |
| — ^d | | | | | |

Table 12.4-4 (cont.).

| Product | Control Device | Particle Size ^a (µm) | Cumulative Mass % ≤ Stated Size | Cumulative Mass Emission Factor (kg/Mg alloy) | EMISSION FACTOR RATING |
|---|-------------------------|------------------------------------|---------------------------------------|--|------------------------------|
| SiMn Open furnace (SCC 3-03-006-05) | None ^{b,m} | 0.5 | 28 | 27 | C |
| | | 1.0 | 44 | 42 | |
| | | 2.0 | 60 | 58 | |
| | | 2.5 | 65 | 62 | |
| | | 4.0 | 76 | 73 | |
| | | 6.0 | 85 | 82 | |
| | | 10.0 | 96 ^k | 92 ^k | |
| | — ^d | 100 | 96 | | |
| | Scrubber ^{m,n} | 0.5 | 56 | 1.18 | C |
| | | 1.0 | 80 | 1.68 | |
| | | 2.0 | 96 | 2.02 | |
| | | 2.5 | 99 | 2.08 | |
| | | 4.0 | 99.5 | 2.09 | |
| | | 6.0 | 99.9 ^k | 2.10 ^k | |
| 10.0 | | 100 | 2.1 | | |

^a Aerodynamic diameter, based on Task Group On Lung Dynamics definition.
Particle density = 1 g/cm³.

^b Includes tapping emissions.

^c References 4,10,21.

^d Total particulate, based on Method 5 total catch (see Tables 12.4-2 and 12.4-3).

^e Includes tapping fumes (estimated capture efficiency 50%).

^f References 4,10,12.

^g References 10,13.

^h Includes tapping fumes (estimated capture efficiency 60%).

^j References 1,15-17.

^k Interpolated data.

^m References 2,18-19.

ⁿ Primary emission control system only, without tapping emissions.

Table 12.4-5 (English Units). SIZE-SPECIFIC EMISSION FACTORS FOR SUBMERGED ARC FERROALLOY FURNACES

| Product | Control Device | Particle Size ^a (μm) | Cumulative Mass % \leq Stated Size | Cumulative Mass Emission Factor (lb/ton alloy) | EMISSION FACTOR RATING |
|---|-----------------------|---|--|---|------------------------------|
| 50% FeSi Open furnace (SCC 3-03-006-01) | None ^{b,c} | 0.63 | 45 | 32 | B |
| | | 1.00 | 50 | 35 | |
| | | 1.25 | 53 | 37 | |
| | | 2.50 | 57 | 40 | |
| | | 6.00 | 61 | 43 | |
| | | 10.00 | 63 | 44 | |
| | | 15.00 | 66 | 46 | |
| | | 20.00 | 69 | 48 | |
| | — ^d | 100 | 70 | | |
| | Baghouse | 0.63 | 31 | 0.56 | B |
| | | 1.00 | 39 | 0.70 | |
| | | 1.25 | 44 | 0.80 | |
| | | 2.50 | 54 | 1.0 | |
| | | 6.00 | 63 | 1.1 | |
| 10.00 | | 72 | 1.3 | | |
| 15.00 | 80 | 1.4 | | | |
| 20.00 | 85 | 1.5 | | | |
| | | 100 | 1.8 | | |
| 80% FeMn Open furnace (SCC 3-03-006-06) | None ^{e,f} | 0.63 | 30 | 8 | B |
| | | 1.00 | 46 | 13 | |
| | | 1.25 | 52 | 15 | |
| | | 2.50 | 62 | 17 | |
| | | 6.00 | 72 | 20 | |
| | | 10.00 | 86 | 24 | |
| | | 15.00 | 96 | 26 | |
| | | 20.00 | 97 | 27 | |
| | — ^d | 100 | 28 | | |
| | Baghouse ^e | 0.63 | 20 | 0.10 | B |
| | | 1.00 | 30 | 0.14 | |
| | | 1.25 | 35 | 0.17 | |
| | | 2.50 | 49 | 0.24 | |
| | | 6.00 | 67 | 0.32 | |
| 10.00 | | 83 | 0.40 | | |
| 15.00 | 92 | 0.44 | | | |
| 20.00 | 97 | 0.47 | | | |
| — ^d | 100 | 0.48 | | | |

Table 12.4-5 (cont.).

| Product | Control Device | Particle Size ^a (µm) | Cumulative Mass % ≤ Stated Size | Cumulative Mass Emission Factor (lb/ton alloy) | EMISSION FACTOR RATING |
|--|--------------------|------------------------------------|---------------------------------------|---|------------------------------|
| Si Metal ^g Open Furnace (SCC 3-03-006-04) | None ^h | 0.63 | 57 | 497 | B |
| | | 1.00 | 67 | 584 | |
| | | 1.25 | 70 | 610 | |
| | | 2.50 | 75 | 654 | |
| | | 6.00 | 80 | 698 | |
| | | 10.00 | 86 | 750 | |
| | | 15.00 | 91 | 794 | |
| | | 20.00 | 95 | 828 | |
| | — ^d | 100 | 872 | | |
| | Baghouse | 1.00 | 49 | 15.7 | B |
| | | 1.25 | 53 | 17.0 | |
| | | 2.50 | 64 | 20.5 | |
| | | 6.00 | 76 | 24.3 | |
| | | 10.00 | 87 | 28.0 | |
| | | 15.00 | 96 | 31.0 | |
| 20.00 | | 99 | 31.7 | | |
| — ^d | | 100 | 32.0 | | |
| FeCr (HC) Open furnace (SCC 3-03-006-07) | None ^{bj} | 0.5 | 19 | 30 | C |
| | | 1.0 | 36 | 57 | |
| | | 2.0 | 60 | 94 | |
| | | 2.5 | 63 ^k | 99 | |
| | | 4.0 | 76 | 119 | |
| | | 6.0 | 88 ^k | 138 | |
| | | 10.0 | 91 | 143 | |
| | | — ^d | 100 | 157 | |
| | ESP | 0.5 | 33 | 0.76 | C |
| | | 1.0 | 47 | 1.08 | |
| | | 2.0 | 67 | 1.54 | |
| | | 2.5 | 80 | 1.84 | |
| | | 4.0 | 86 | 1.98 | |
| | | 6.0 | 90 | 2.07 | |
| | | 10.0 | 100 | 2.3 | |
| — ^d | | | | | |

Table 12.4-5 (cont.).

| Product | Control Device | Particle Size ^a (µm) | Cumulative Mass % ≤ Stated Size | Cumulative Mass Emission Factor (lb/ton alloy) | EMISSION FACTOR RATING |
|---|-------------------------|------------------------------------|---------------------------------------|---|------------------------------|
| SiMn Open furnace (SCC 3-05-006-05) | None ^{b,m} | 0.5 | 28 | 54 | C |
| | | 1.0 | 44 | 84 | |
| | | 2.0 | 60 | 115 | |
| | | 2.5 | 65 | 125 | |
| | | 4.0 | 76 | 146 | |
| | | 6.0 | 85 | 163 | |
| | | 10.0 | 96 ^k | 177 ^k | |
| | — ^d | 100 | 192 | | |
| | Scrubber ^{m,n} | 0.5 | 56 | 2.36 | C |
| | | 1.0 | 80 | 3.34 | |
| | | 2.0 | 96 | 4.03 | |
| | | 2.5 | 99 | 4.16 | |
| | | 4.0 | 99.5 | 4.18 | |
| | | 6.0 | 99.9 ^k | 4.20 ^k | |
| 10.0 | | 100 | 4.3 | | |

^a Aerodynamic diameter, based on Task Group On Lung Dynamics definition.
Particle density = 1 g/cm³.

^b Includes tapping emissions.

^c References 4,10,21.

^d Total particulate, based on Method 5 total catch (see Tables 12.4-2 and 12.4-3).

^e Includes tapping fumes (estimated capture efficiency 50%).

^f References 4,10,12.

^g References 10,13.

^h Includes tapping fumes (estimated capture efficiency 60%).

^j References 1,15-17.

^k Interpolated data.

^m References 2,18-19.

ⁿ Primary emission control system only, without tapping emissions.

Available data are insufficient to provide emission factors for raw material handling, pretreatment, and product handling. Dust particulate is emitted from raw material handling, storage, and preparation activities (see Figure 12.4-1). These activities include unloading raw materials from delivery vehicles (ship, railway car, or truck), storing raw materials in piles, loading raw materials from storage piles into trucks or gondola cars, and crushing and screening raw materials. Raw materials may be dried before charging in rotary or other types of dryers, and these dryers can generate significant particulate emissions. Dust may also be generated by heavy vehicles used for loading, unloading, and transferring material. Crushing, screening, and storage of the ferroalloy product emit particulate matter in the form of dust. The properties of particulate matter emitted as dust are similar to the natural properties of the ores or alloys from which they originated, ranging in size from 3 to 100 micrometers (µm).

Approximately half of all ferroalloy facilities have some type of control for dust emissions. Dust generated from raw material storage may be controlled in several ways, including sheltering storage piles from the wind with block walls, snow fences, or plastic covers. Occasionally, piles are sprayed with water to prevent airborne dust. Emissions generated by heavy vehicle traffic may be reduced by using a wetting agent or paving the plant yard. Moisture in the raw materials, which may be as high as 20 percent, helps to limit dust emissions from raw material unloading and loading. Dust generated by crushing, sizing, drying, or other pretreatment activities may be controlled by dust collection equipment such as scrubbers, cyclones, or fabric filters. Ferroalloy product crushing and sizing usually require a fabric filter. The raw material emission collection equipment may be connected to the furnace emission control system. For fugitive emissions from open sources, see Section 13.2 of this document.

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PLASMA TECHNOLOGY IN FERROALLOY PROCESSING

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Introduction

Plasma technology has come a long way since the early reported applications to metallurgy by Sir W. Siemens (1878) and H. Moissan (1897) about a century back [1]. Major attraction of using plasma in metallurgical smelting operations, especially in the last two to three decades, have emerged from its ability to deliver high grade heat to any environment independently of oxygen potential. Furthermore, compact unit of high throughput, due to high power flux and higher reaction rates attained, and ability to handle cheaper fine feed without causing pollution problems have been the other important attractions. Although, the development of plasma technology in the area of nonferrous extractive metallurgy is still confined to the laboratory and pilot plant research stage, applications in ferrous metallurgy have entered the stage of commercialization. Table 1 lists some of the high capacity iron and steel installations. Ferroalloys production, using carbothermic smelting reduction of oxide ores and by remelting of ferroalloys fines, has been a major driving force in fostering the development of plasma technology. As indicated in Table 1, both ferro manganese and ferro chromium are being produced at present on industrial scale. Research and development in the production of other ferroalloys, e.g. ferro silicon, ferro vanadium, ferro molybdenum, is in an advanced stage.

A brief review is presented in this paper on the application of plasma technology for ferroalloys production. We begin with the definition of plasma in general, followed by a discussion on various plasma furnaces, process fundamentals, i.e. chemistry and transport phenomena in plasma environment, and energy considerations involved in plasma smelting. Finally, the advantages of the technology, vis-a-vis the conventional processing using submerged arc furnace, and relevance of the technology in the Indian context are brought into focus. Specific examples of ferroalloys are cited wherever possible. The reader may refer to the reviews [1-6] for detail.

Plasma - A Basic Definition

Reckoned as the fourth state of matter, a plasma is essentially an ionized gas which may comprise molecules, atoms, ions (in ground or excited state), electrons and protons, and is sufficiently ionized to become electrically conductive. Overall, a plasma maintains electrical neutrality, i.e. the property of quasineutrality. Unlike an ordinary gas, a plasma contains free electric charge which may be produced by a variety of ionization processes, e.g., high energy radiation, such as, UV, X-ray etc., collision processes in intensely heated gas electrodeless RF discharge, microwave, shockwave, laser beam, or simply electrical arc discharge. It is the last process which is of interest in generating plasma for ferroalloys production.

A plasma can be of two types - the equilibrium or thermal or hot plasma and the nonequilibrium or cold plasma. In the former, the temperature of the electrons is close to that of heavy particles and chemical equilibrium prevails. In the later, the electron temperature is far above the sensible

temperature of heavy particles, which is closer to room temperature. Plasma produced by high intensity electric arc, as in the ferroalloys production, falls in the category of thermal plasma. Although, the temperature in the case of thermal plasma ranges from 2000 to 20000 K, most processes of practical interest operate between 4000 to 7000 K.

Plasma Furnaces for Ferroalloys Smelting

Like any conventional electric arc furnace, a large scale commercial thermal plasma device operates on the basis of a high intensity electric arc discharge originating from a cathode and terminating at an anode. Several reviews on plasma furnaces are available in literature [1,2,5-9]. A general description of plasma furnaces used for the smelting of ferroalloys is presented here.

Depending upon the way the arc is struck, the state of the feed material, as well as, its handling strategy, plasma systems are broadly classified into the following three categories : (a) nontransferred arc plasma; (b) transferred arc plasma; and (c) in-flight plasma. Nontransferred arc plasma system, normally designed to heat gases, consists of two electrodes in which one of the electrodes may be tubular type from which the hot gas emerges (Fig.1a). In the transferred arc plasma system, one of the electrodes is in the plasma torch and the material to be heated or melted acts as the second electrode (Fig. 1b). The in-flight plasma system involves the feeding of raw materials (completely or partially) within the plasma to utilize the thermal and reduction potential of plasma flame (Fig.1c). As listed in Table 2, a number of reactor designs have emerged for the smelting of ferroalloys depending upon the configuration of plasma systems in the furnace. Some typical furnaces are schematically shown in Figure 2. MINTEK open bath furnace (Fig. 2a) and University of Minnesota in-flight plasma reactor (Fig. 2b) make use of transferred arc and in-flight plasma system, respectively. The design of Hydro-Qubec-Noranda reactor, as adopted in Davy McKee Hi-plas furnace (Fig.2c), the reactor developed by ASEA, Tetronics plasma furnace and Bethlehem Steel falling film reactor, make use of both transferred arc and in-flight systems. The extended arc flash reactor (EAFR) (university of Toronto) includes in-flight gas reduction and as well as melt heating by plasma fire ball generated using non-transferred arc system (Fig 2d). SKF design make use of a shaft furnace in which nontransferred plasma system is used essentially for heating the gases. In recent years transferred arc system, using in-flight reduction and bath smelting, have received considerable attention and will be the point of focus in the following sections.

Process Chemistry Consideration

The application of thermodynamic and kinetic principles in the extraction of metals using plasma has been found to be of prime importance. In this respect, chemical driving force and energy balances determined using ΔG and ΔH considerations, the use of acidic or basic slag recipes and study of reaction mechanisms and process stages have all been found to be vital in the refinement and advancement of plasma reactor engineering and design [9,10].

Thermodynamics

Coal or carbon based reductants are potentially the most economical to use with a plasma reactor. Thermodynamic principles described in an earlier chapter apply for the carbothermic reduction of metal oxides in plasma reactor too. Some salient points, relevant to the processing of ferroalloys in plasma environment, are presented here. Thermodynamically, metal oxide reduction

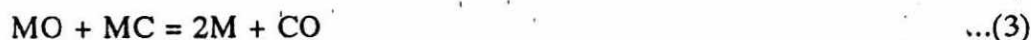
with a carbon based reductant can be represented by the following reaction :



However for more stable oxides than FeO, as the temperature is increased, metal carbide formation by



is thermodynamically more feasible than elemental metal (Fig.3a-b). The metal carbide can also participate in the reduction of metal oxide according to the reaction given below :



The reaction (3) generally has the highest free energy of formation and requires a higher temperature than for direct metal formation (1). Table 3 lists the minimum temperature (temperature corresponding to $\Delta G = 0$) for reaction (1), (2) and (3). For carbothermic reduction in a plasma reactor, a further criterion is that the reactor temperature is not only greater than the minimum (i.e. $\Delta G = 0$) temperature but the melting point T_m of metal (or the temperature at which the metal dissolves in the Fe-C melt) and the slag formation temperature. The data presented in Table 4 indicate that, in general, the minimum reactor temperature is dictated by the minimum ($\Delta G = 0$) temperature.

Since carbide formation is favoured at higher temperature for metals which form more stable oxide than Fe_2O_3 and metal formation by reaction (3) requires a very high temperature, plasma smelting is more suitable for the production of bulk carbide or high carbon ferroalloys. Plasma environment, especially in the in-flight mode, may be ideal for the production of low sulfur and low phosphorus ferroalloys. This may be due to the vaporization of sulfur or phosphorus compounds and early slag formation under high temperature. Stable gaseous compound, e.g. SiS (ΔG° at 2000K = -28 kcal/mol) at the slag surface in the absence of any basic flux and likelihood of the formation and volatilization of CaS ($\Delta G^\circ = -76$ cal/mol at 2000K) and Na_2S ($\Delta G^\circ = -76$ cal/mol at 2000K) may facilitate S removal in plasma environment [9,10].

Kinetics and Mechanisms

Plasma environment provides some unique conditions which are favourable for the reduction of mineral oxides with carbon based reductants : the plasma is in nonequilibrium conditions, i.e. electron temperatures are much higher than the heavy species, e.g. ions; gaseous molecules and atoms are present in very reactive states; and a significant degree of ionization of species exists. Such conditions make any proposed mechanism(s) of metal oxide reduction in plasma environment highly speculative. The mechanism(s) for in-flight plasma reduction, which involves intimate plasma particle interaction, are expected to be more complex than bath-smelting using plasma.

In-flight Plasma Reduction : Particles are subjected to steep temperature (1000-10000K) and velocity (100-400 m/s) gradient during flight in plasma flame (Fig 4) [11,12]. Since the residence time of particles in the plasma is small (few milliseconds), complete reduction of particles is not

achieved during in-flight. Due to high temperatures, the particles undergo melting and vaporization to different degrees depending upon size and their physical properties. Chemical reactions, e.g. gasification, reduction and slag formation, involving different combinations of solid, liquid and gaseous phases can also take place simultaneously [13,14].

Carbothermic reduction of metal oxides in plasma environment, like that in conventional process, occurs via the kinetically more favourable gaseous reductant CO, i.e.



and the Boudouard (C gasification) reaction is the rate controlling reaction, i.e.,

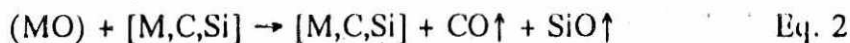
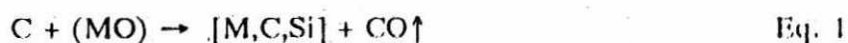


Addition of reaction (4) and (5) results in overall thermodynamic reaction (1). Under certain circumstances a small amount of oxygen may need to be injected in order to initiate and sustain gasification reaction and carbothermic reduction process under plasma.

There have been some attempts to analyze the reaction product of in-flight reduction, by X-ray, SEM-EDS and electron microprobes, and conjecture the reduction mechanism(s) for the reduction of chromite and taconite [14]. Two reduction mechanisms have been postulated based on the production of microchannels of plasma in larger mineral particles, e.g. greater than 100 μm for chromite (Fig.5a), and the formation, slag-metal microcells in the finer mineral particles, e.g., less than 50 μm for taconite (Fig.5b). Microchannels of plasma in large particles, produced due to outgassing through microcracks or channels developed on being subjected to the turbulent plasma medium and very high heating rates, are proposed to act as highly reactive areas along which reduction of mineral is initiated giving rise to fine spherules of liquid metallics. Given sufficient time within the plasma and continued efficient plasma particle interaction, these liquid metallic spherules coalesce in order to reduce their surface energy, eventually forming large spherules and globules of reduced metallics saturated with carbon. The smaller mineral particles tend to melt completely on introduction into the plasma medium, thereby partly or completely inhibiting the formation of microchannels of plasma within the particles. In this condition very fine slag-metal microcells are established within the plasma. Such microcells provide favourable reduction kinetics and as such effect the necessary reduction reactions producing metallic products embedded in a slag phase. The slag phase will be controlled by the composition of the ore and any flux additions, e.g. SiO_2 or CaO , made to the feed material. Since the metallic phase will usually have higher melting point than the slag phases, the metallic phase will solidify first and will be surrounded by a slag phase. It is also likely that reduction of mineral, e.g. Fe_3O_4 , will proceed through one or several intermediate stages during reduction, e.g., Fe_3O_4 - FeO - Fe . Therefore, it may be expected to find the metallic phase situated predominantly in a partially reduced mineral or slag phase.

The limiting particle size which determines which of these reduction mechanisms predominates is likely to depend on the thermal and physical properties of the mineral, and it is also feasible that both of these mechanisms may operate within a mineral system.

Open Bath Smelting : Kinetics considerations, which are relevant to the conventional processing in submerged arc bath, are also applicable during plasma processing. The transfer of heat from plasma arc to the bath and bath circulation has been modelled by Szekely [11]. A large proportion of plasma energy is dissipated in the high temperature pumped gas diverging from the anode attachment region; and in a contained furnace environment, a complex interaction of the convective component, the radiative component, the evolved process gases and the liquid slag bath would be expected. Figure 6 illustrates the general arrangement of an open bath plasma furnace and behavior of the various feed particles in the liquid slag. Equations 1-3 marked in figure correspond to the carbothermic reduction of a metal oxide, in the presence of a silicate slag, as exemplified below :



Mass transport and kinetics of reaction will very strongly depend on the local temperature, and given the high temperature, high power-density nature of plasma arcs, large temperature gradients are the essential feature of bath smelting configuration. Use of only the surface of the slag in the furnace as the reaction zone imposes a constraint on the reaction rates. The distribution of the feed particles throughout the slag volume would be expected to greatly increase the reaction kinetics and, consequently, capability of the furnace to accept higher feed rates. Such distribution could be achieved in a number of ways, e.g. by stirring of the bath with inert gas, pneumatic injection of the feed material into the bath via a vertical lance, or bottom or side tuyeres, electromagnetic stirring of the bath etc [6,15].

Slag Chemistry

During smelting in conventional submerged arc furnace; the dual functions of slag as electrical load and as chemical reaction site are not complimentary in specific cases, e.g. smelting of ferro manganese. An acid slag ($SiO_2+Al_2O_3$) is more resistive and is required for effective energy input and higher production rates. On the contrary, a basic slag ($CaO+MgO$) increases the activity of iron and manganese oxide in the slag phase and, consequently, promotes reduction and results in higher yields. This problem is overcome in a plasma furnace because energy input to a plasma furnace is not dependent on the slag resistivity and, therefore, slag chemistry can be optimized for reduction reactions. Typically, for the smelting of a manganese ore from South Africa in a transferred arc DC plasma furnace at MINTEK, the basicity was varied between 1.3 and 1.5 and the corresponding values of the manganese distribution to the metal/slag/vapour phases were found to be 63/20/17 and 79/10/11, respectively. The MnO content of the slag at 1.5 basicity decreased to about 10 percent compared to about 30 percent for conventional submerged arc operations [1].

Energy Related Issues

Power Input and Furnace Type

Power delivered to an arc furnace is the product of current and voltage. Figure 7 shows the

current, voltage and power relationships for some typical commercial plasma arc systems, used in ferroalloy furnaces, from high current low voltage end to low current high voltage end. The operating voltage of nontransferred plasma torches (AC or DC), e.g. as used in the gas heater for SKF shaft furnace, are higher than for transferred arc torches. DC transferred arc technology is widely preferred for metallurgical processing, e.g. ferroalloy smelting. DC transferred arc furnace using non cooled hollow graphite electrode, e.g. MINTEK furnace, operates at higher current and power level as compared to water cooled tungsten cathode, e.g. Tetronics Design, furnace.

Energy Requirement and Distribution

The gross energy required for plasma smelting includes the following components :

- 1) The net energy required for reduction reaction, i.e. the energy required to heat the reactants to the reactor temperature plus energy for any change of state (e.g. solid to liquid changes, coal devolatilization etc) and heat of reaction
- 2) Energy required to heat any nonreactant gas used for arc stabilization, gases for conveying the solids, slag additives, cooling water for arc heater electrodes and losses to the crucible.

The energy requirement (excluding losses), which is of the order of 0.5 MWh/t for the melting of scrap, may vary between 3 to 8 MWh/t for the ferroalloys [5]. Figure 8 shows the power distribution for the processing of high carbon ferro manganese fines in a Hi-plas Davy McKee furnace. About 80% arc power may be utilized by the process energy (sum of sensible heat and energy involved in the chemical reaction) [16]. Percentage contribution of reaction energy increases with increase in the oxygen content of fines. During production of ferroalloys, the heat of reaction is a substantial fraction of the net energy and may equal to the energy required to heat the feed upto the reactor temperature. The capacity of a plasma heater to provide a high heat flux at high reaction temperature is an important factor that can minimize the capital and operating costs of a plasma reactor compared to other reactor (Fig.9).

Energy Efficiency

It has been found that at the same throughput rate and power flux, the efficiency of open bath plasma furnace is lower than that of a submerged-arc furnace. Factors responsible for this are:

- 1) more energy is lost, by radiation from open arc and molten bath, to the wall and roof of the furnace,
- 2) some vaporized material is lost to the off-gas stream from the arc attachment zone, and
- 3) little of the sensible energy of the gases evolved is utilized in preheating.

The energy efficiency is directly related with the throughput rate (Fig.10) and can be increased by increasing the throughput rate. Plasma furnaces in which both in-flight mode and open bath configurations are coupled also shows higher efficiency. It has been further observed that integration of prerduction/preheating step with a plasma smelting process can also result in considerable improvement in energy efficiency. For the smelting of South African manganese ores for the production of high C ferro manganese in a Noranda type plasma reactor (Fig 3c), researchers at Davy McKee has reported that ore pretreatment results in reduction of approximately 45% in electrical energy and 35% coke over the process in which no ore pretreatment is carried out; energy required with and without treatment were 2100 kWh/t and 3850 kWh/t, respectively [17]. The integrated ore reduction pretreatment and plasma smelting process consumes only 2100 kWh/t energy in comparison with conventional submerged arc-furnace which consumes 3100-3200 kWh/t for a similar ferroalloy and slag composition and no recovery of the energy from furnace gas [17].

Advantages Over Conventional Process

The production of ferroalloys by plasma technique offer several advantages over smelting in conventional submerged arc furnace :

- a) no need for costly sizing, screening and agglomeration of fines.
- b) no problems due to electrical conductivity of the carbonaceous reducing agent and the slag, since the plasma furnace operation is not affected by an uncontrollable rate of descent of the feed in the hot zone, as in an electric furnace.
- c) much lower cost of installation of power supply for plasma furnace (typical figure are \$ 165 and 360 per installed kilowatt for plasma and conventional furnace, respectively).
- d) no need for very large vessels to accommodate the large volume of unreacted burden.
- e) no need for lumpy metallurgical coke; any carbonaceous reducing agent can be used, provided it will not contribute to undesirable impurities in the product.
- f) trivial cost of replacement (including down-time) compared to cost of consumable cathode used in arc furnaces, despite the fact that the cathode used in transferred-arc furnaces have a limited life (200-400 h)
- g) no flicker on the power grid
- h) little noise and gaseous pollution and less environmental problems

Relevance in the Indian Context

The ferroalloy industry in India is characterized by low capacity utilization. Any further addition in capacity based on a new process flow sheet, using existing or new raw materials, is unlikely in near future. The electrical supply characteristics and geometric arrangement of the transferred arc plasma furnace with graphite electrode are similar to conventional submerged arc furnaces and change to DC plasma furnace operations is relatively straightforward. For example, the modification or retrofit of an existing MSA submerged arc furnace , used for ferro chromium production, has been successfully attempted by MINTEK in South Africa. For a retrofit process the economic advantage will be primarily in lower costs of raw materials, improved furnace operations and in higher yield. In comparison to submerged arc furnaces, it will be possible to use cheaper ores or oxide concentrates and cheaper reductant. There will be furnace savings from decreased electrode consumption and smoother electrical operations and improved furnace control.

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Table 1 : Commercially Operating Plasma Installations for Iron and Steel Production

| Product | Company | Process | Capacity | |
|-----------------------|---|---|-----------------------|--------|
| | | | MW 10 ⁴ | tpa |
| Iron Direct Reduction | SKF Sweden | SKF Torches Gas Reforming | 6 | 7 |
| Iron Direct Reduction | USCO South Africa | Huels Torches Gas Reforming | 3x8 | 3 2 |
| Pig Iron | SKF Sweden | Coke-Filled Shaft SKF Torches | 7x6 | 2 5 |
| Pig Iron | ASEA South Africa | Transferred Arc Graphite Cathode | 40 | 6 0 |
| Steel | Mannesmann, GHH, Germany | Transferred Arc Graphite Cathode | 6 | - |
| Steel | ASEA/Krupp, Germany | Transferred Arc Graphite Cathode | 18 | - |
| Steel | V E Freital, Germany | Transferred Arc Multiple Torches | 3x3 | - |
| Steel | V E Freital, Germany | Transferred Arc Multiple Torches | 4x3 | - |
| Steel | Voest Alpine, Linz, Austria | Transferred Arc Multiple Torches | 4x7 | - |
| Ferro-Chrome | Middleburg Steel and Alloy South Africa | Transf. Arc Hollow Graphite Cathode | 20 | 5 |
| Ferro-Chrome | SKF Sweden | Coke-filled Shaft SKF Torches | 4x6 | 6 |
| Ferro-Manganese | Samancor, South Africa | Transferred Arc | 10.8 | 3 |
| TiO ₂ Slag | Richard's Bay Mining, South Africa | Graphite Electrodes A C Transferred Arc | 6x10 | 5 0 |

Table 2 : List of Different Types of Plasma Reactor, Ferro Alloys for which Used and Originator or User

| Reactor Type | Ferro Alloys For Which Used | Originator/user |
|-----------------------------------|-----------------------------|---|
| DC Transferred arc furnace | FeCr; FeMn, FeMnSi | MINTEK South Africa |
| DC Transferred arc furnace | FeCr | Middleburg Steel and Alloys, (MINTEK, ASEA Desgn) |
| DC Transferred arc furnace | FeCr | ASEA, Vasteras, Sweden |
| DC Transferred arc furnace | FeMn fines | *Samancor, Voest Alpine Design. |
| DC Transferred arc furnace | FeMn fines, FeCr | Davy Mckee, UK (Hydro-Qubec Noranda Design, Canada) |
| DC Transferred arc furnace | FeCr | Tetronics R & D Ltd., UK |
| Falling film reactor | FeCr, FeV | Bethlehem Steel Research Lab., USA |
| Extended arc flash reactor (EAFR) | FeCr dust | University of Toronto, Canada |
| In-flight plasma reactor | FeCr, FeTi | University of Minnesota, USA |
| Coke filled shaft furnace | FeCr, FeMn, FeSi | SKF Sweden |
| | FeCr | Swede Chrome AB Malmo, Sweden |
| Packed bed reactor | FeMn | *SKW Trostberg, Sweden (Voest Alpine Design) |
| Plasma augmented blast furnace | FeMn | SFPO, France |
| RF plasma reactor | FeMo | McGill University, Canada |

Table 3 : Minimum temperature for $\Delta G=0$

| (Ferroalloy production by carbothermic reduction in oxide/carbide/metal system) | | | |
|--|------------------------|----------------------|----------------------|
| Reaction Final Product | (1) Carbide | (2) Metal | (3) Metal |
| System | Temperature °C | | |
| Fe ₂ O ₃ /Fe ₃ C/Fe | 644 | 640 | 571 |
| SiO ₂ /SiC/Si | 1464 | 1551 | 1733 |
| Cr ₂ O ₃ /Cr ₂₃ C ₆ /Cr | 1276 | 1255 | 1734 |
| MnO/M ₇ C ₃ /Mn | 1273 | 1401 | 1762 |
| VO/VC/V | 1048 | 1515 | 1947 |
| Al ₂ O ₃ /Al ₄ C ₃ /Al | 1923 | 2036 | 2271 |
| CaO/Ca ₂ C/C | 1848 | 2152 | 2274 |

Table 4 : Minimum Plasma Reactor Operating Temperatures, T_{Reactor}

| Temperature °C | | | | | | | | |
|-----------------------|-------------------------|----------------------------|--------------------------------|----------------------------|---------------------------|----------|----------------|----------------------------|
| System | T_{ΔG=0} | T_{M,metal} | Oxide | T_{M,oxide} | T_{M,Fe/x} | X | % X | T_{Reactor} |
| Fe | 644 | 1536 | Fe ₃ O ₄ | 1597 | 1147 | C | 4.3 | 1536 |
| Si | 1733 | 1413 | SiO ₂ | 1723 | 1200 | Si | 20 | 1733 |
| Cr | 1734 | 1898 | Cr ₂ O ₃ | 2266 | 1510 | Cr | 20 | 1898 |
| Mn | 1762 | 1244 | MnO ₂ | 1564 | 1232 | Mn | 87 | 1762 |
| V | 1947 | 1912 | V ₂ O ₃ | 1970 | 1470 | V | 30 | 1947 |
| Al | 2271 | 659 | Al ₂ O ₃ | 2050 | 1232 | Al | 42 | 2271 |
| Ca | 2274 | 850 | CaO | 2614 | - | - | - | 2274 |

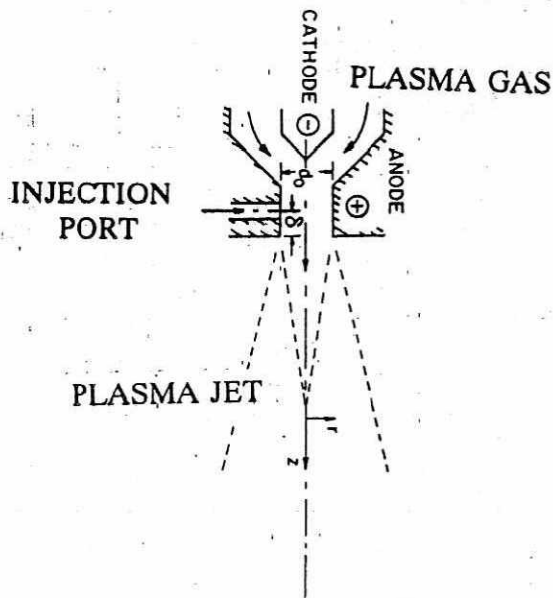
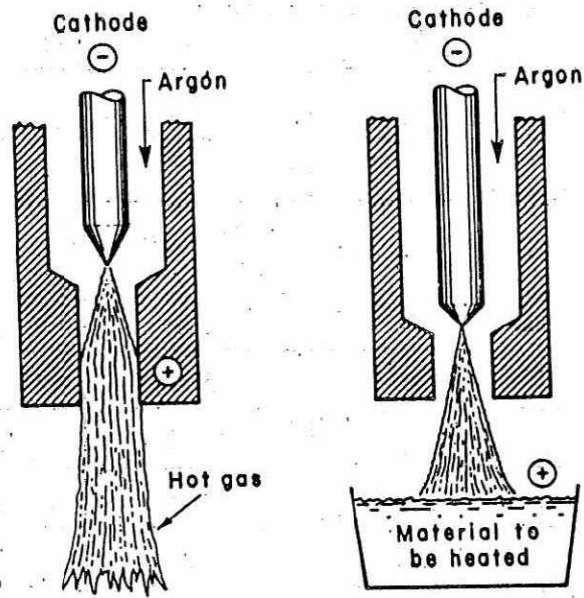
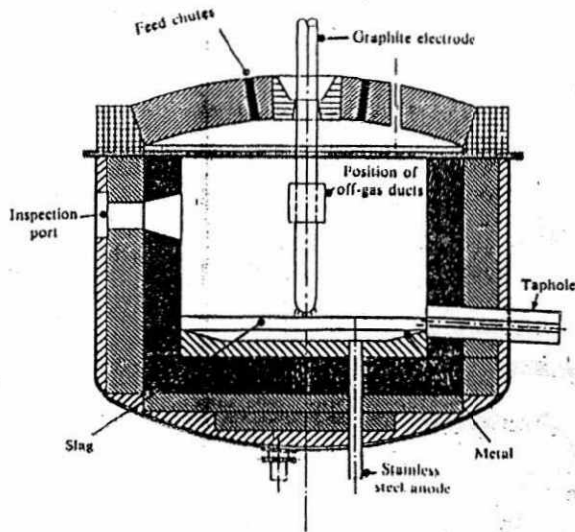


Fig.1 Different kinds of plasma systems
 (a) nontransferred arc plasma [1,p77]
 (b) transferred arc plasma [1,p77]
 (c) in-flight plasma [1,p57]



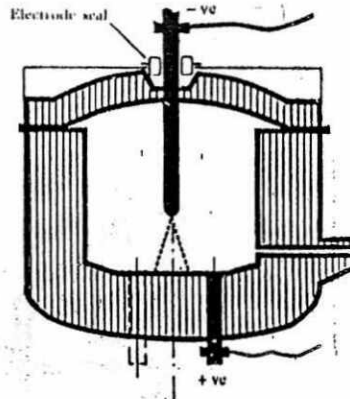
1.0m

| Item | Description |
|------|--|
| | Chemically bonded magnesite ramming (85% MgO) |
| | Chromite-magnesite brick (30% Cr ₂ O ₃) |
| | Tar-impregnated magnesite brick (96% MgO) |
| | Chemically bonded magnesite ramming (96% MgO) |
| | Rammed, fired, and tar-impregnated magnesite |
| | High-alumina castable (90% Al ₂ O ₃) |
| | Magnesite spinel brick (90% MgO) |

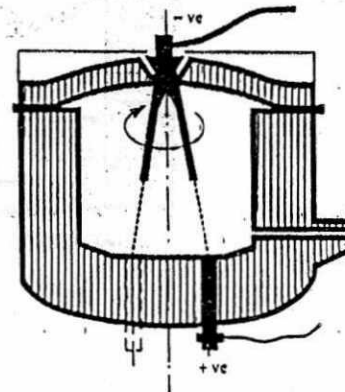
Refractory lining of the 3.2 MVA furnace.

(a)

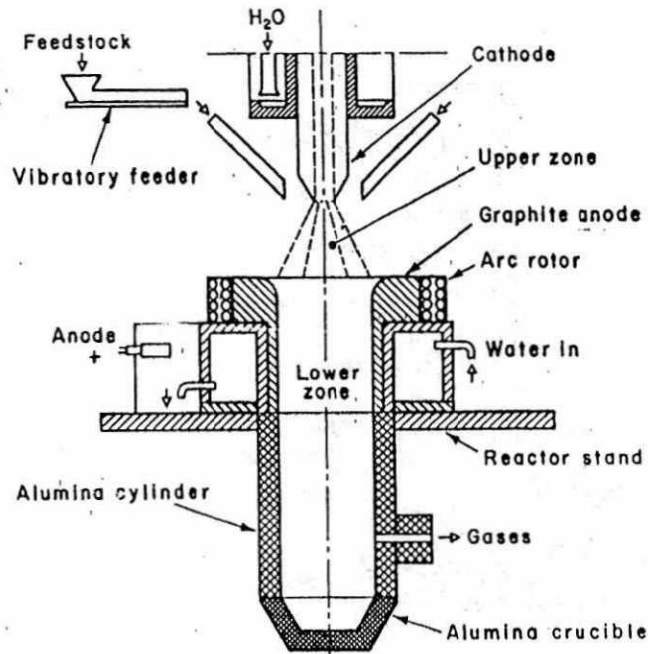
Hollow graphite electrode



Water cooled pressure torch



Alternative plasma torch arrangements.



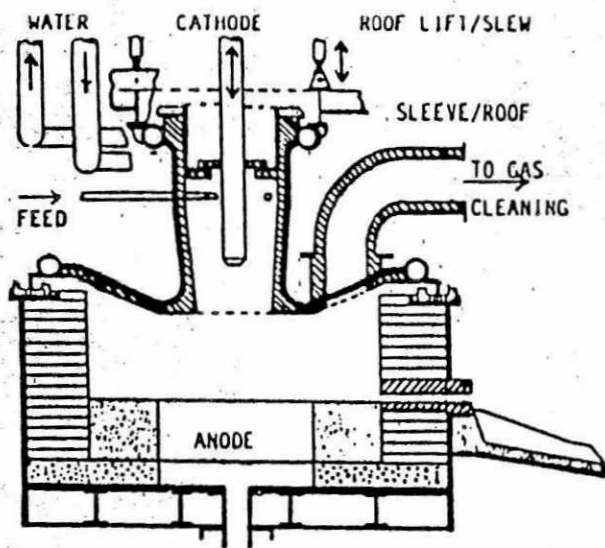
(b)

Fig.2 Schematic diagram of furnaces developed using different kinds of plasma systems

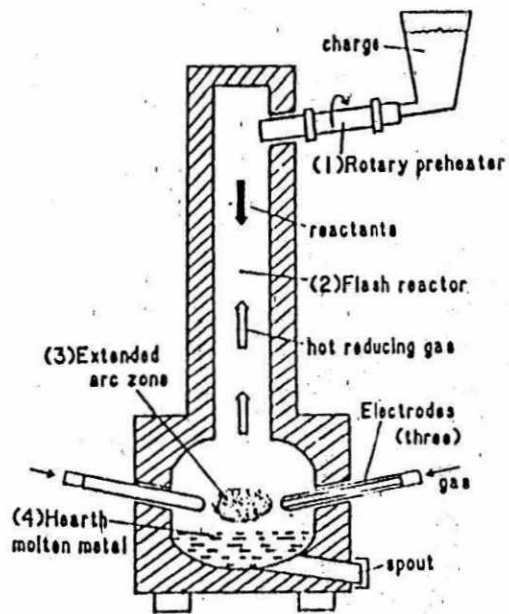
(a) MINTeK open bath furnace [1,p145]

(b) University of Minnesota in-flight plasma reactor [1,p85]

Contd. ...



(c)



(d)

Fig.2 Contd.

(c) Davy McKee Hi-plas furnace [16]

(d) University of Toronto extended arc flash reactor [3]

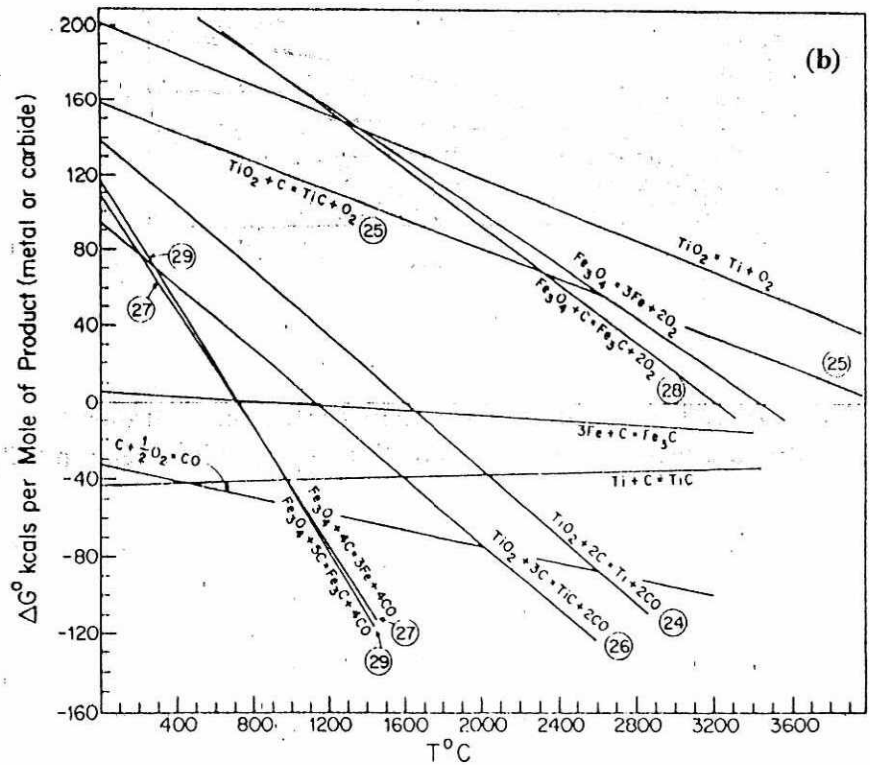
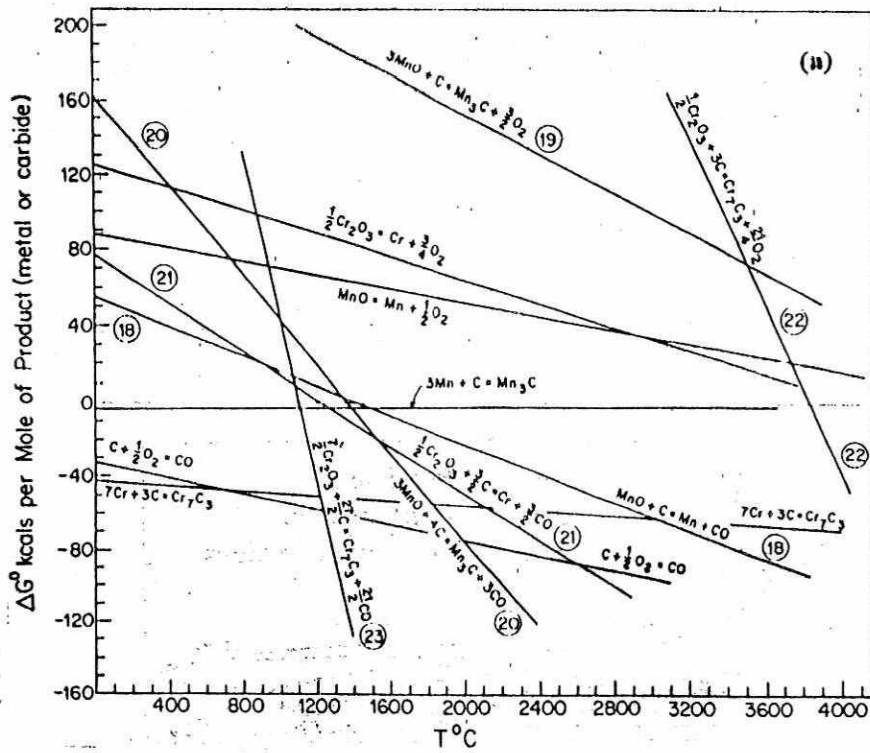


Fig.3 ΔG° -T data for carbothermic reduction of several metal oxides [10]

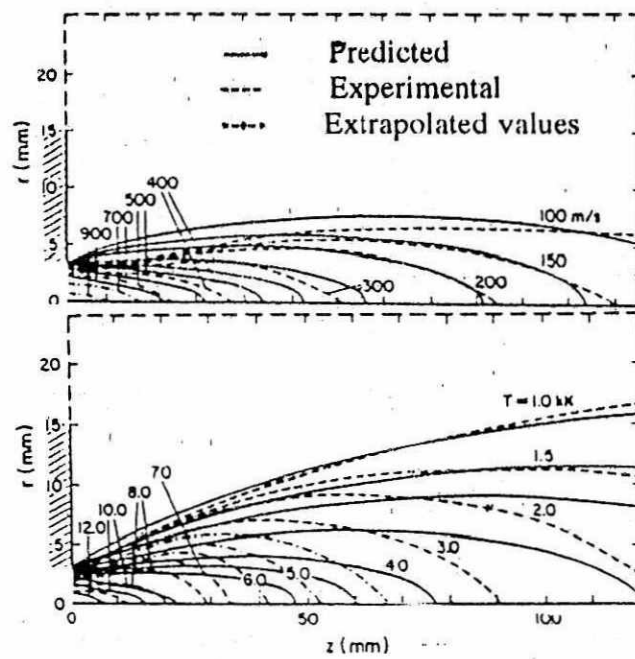


Fig.4 Velocity and temperature isocontours for a typical nitrogen/hydrogen plasma jet; r-radial direction and z-axial direction [12]

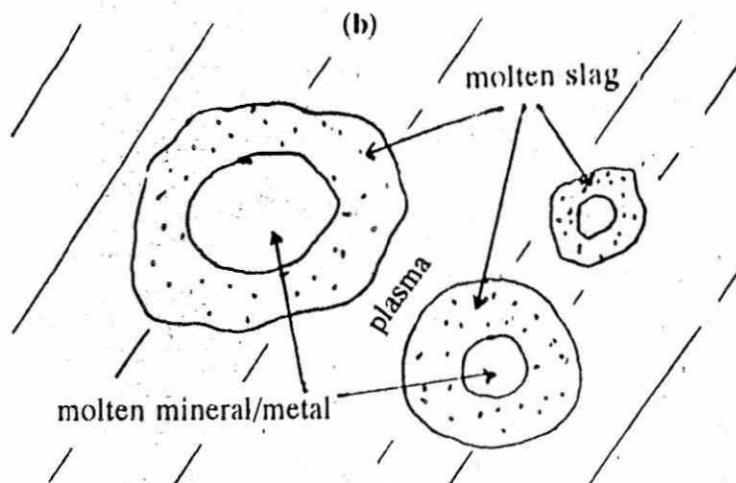
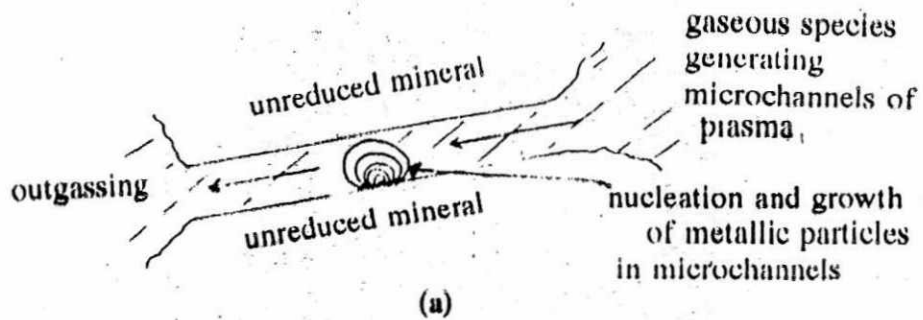


Fig.5 Schematic representation of mechanisms, for the reduction of minerals in an in-flight plasma reactor, based on :
 (a) production of microchannels of plasma in large mineral particles; and
 (b) formation of slag-metal microcells in finer mineral particles which may tend to melt completely on introduction into the plasma medium

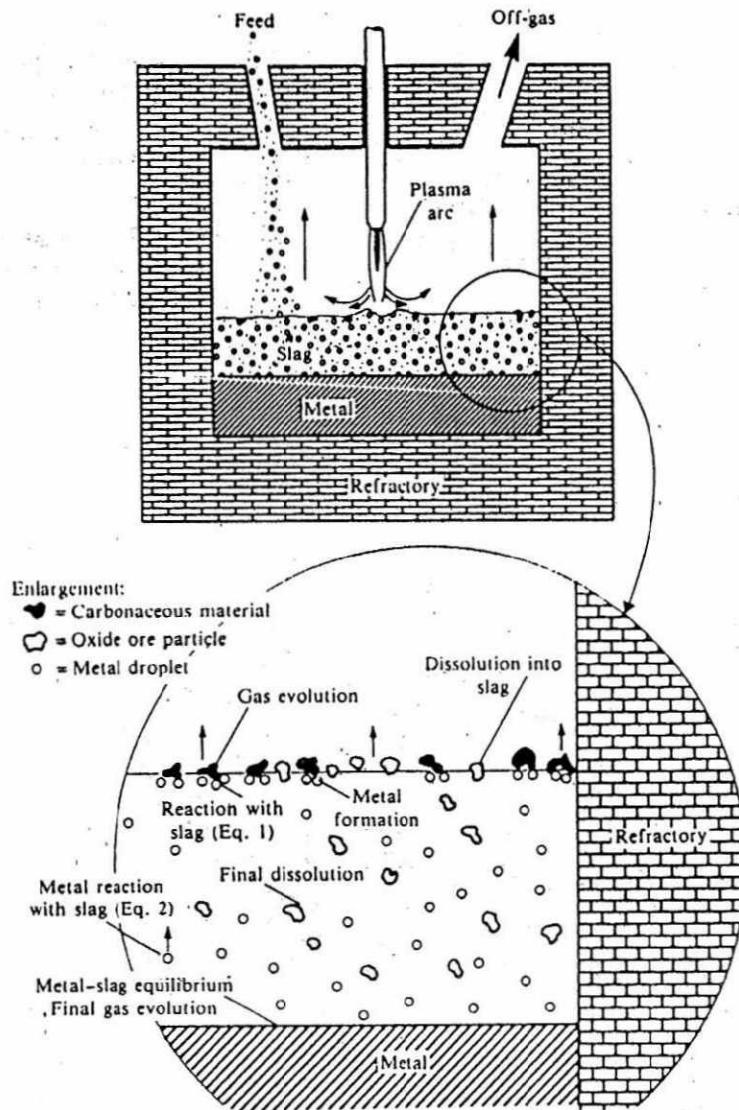


Fig.6 General arrangement of an open bath plasma furnace and behaviour of various feed particles in liquid slag [6]

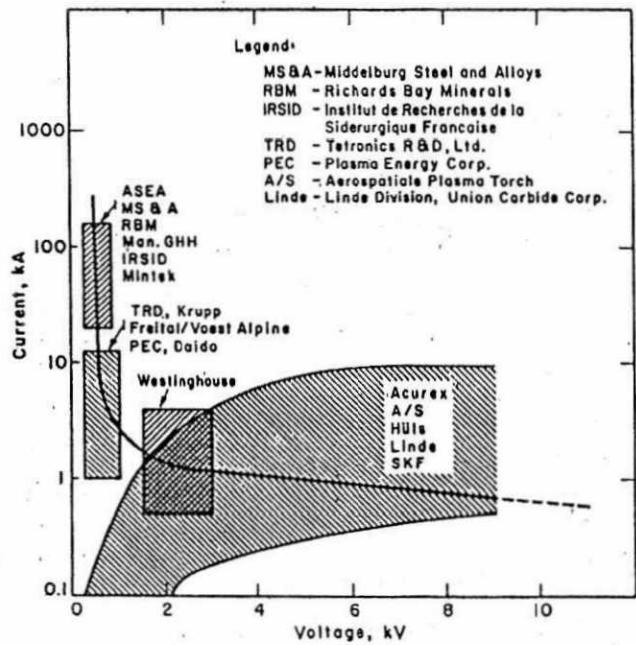


Fig.7 Current voltage and power relationship for some commercial plasma arc systems [1,p81]

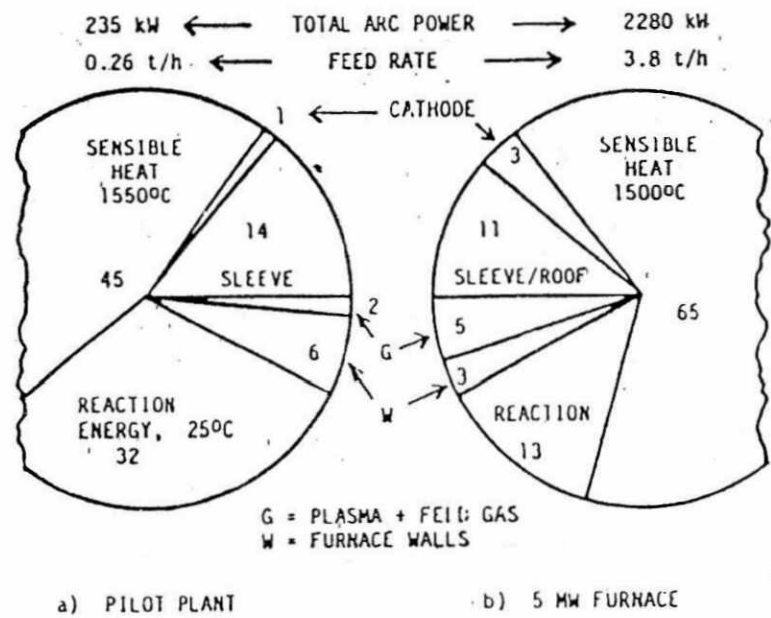


Fig.8 Power distribution for the processing of high carbon ferro manganese fines in a Davy McKee Hi-plas furnace [16]

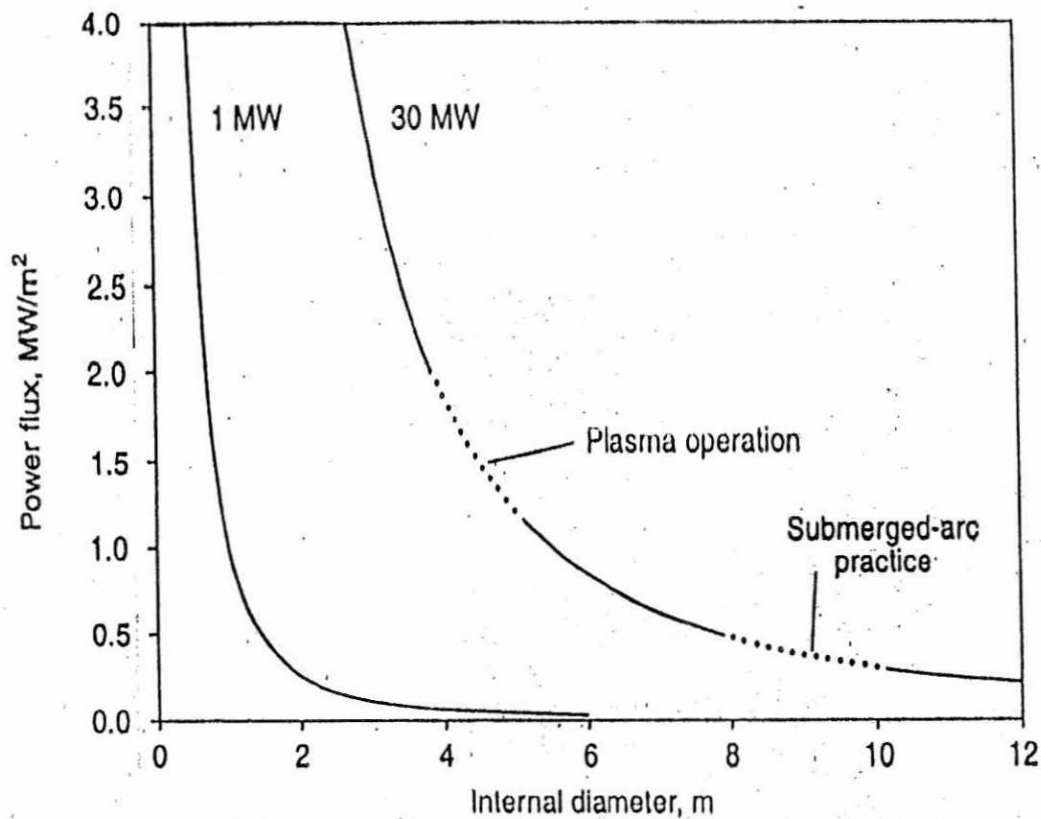


Fig.9 The relationship between power flux and internal diameter of a furnace [5]

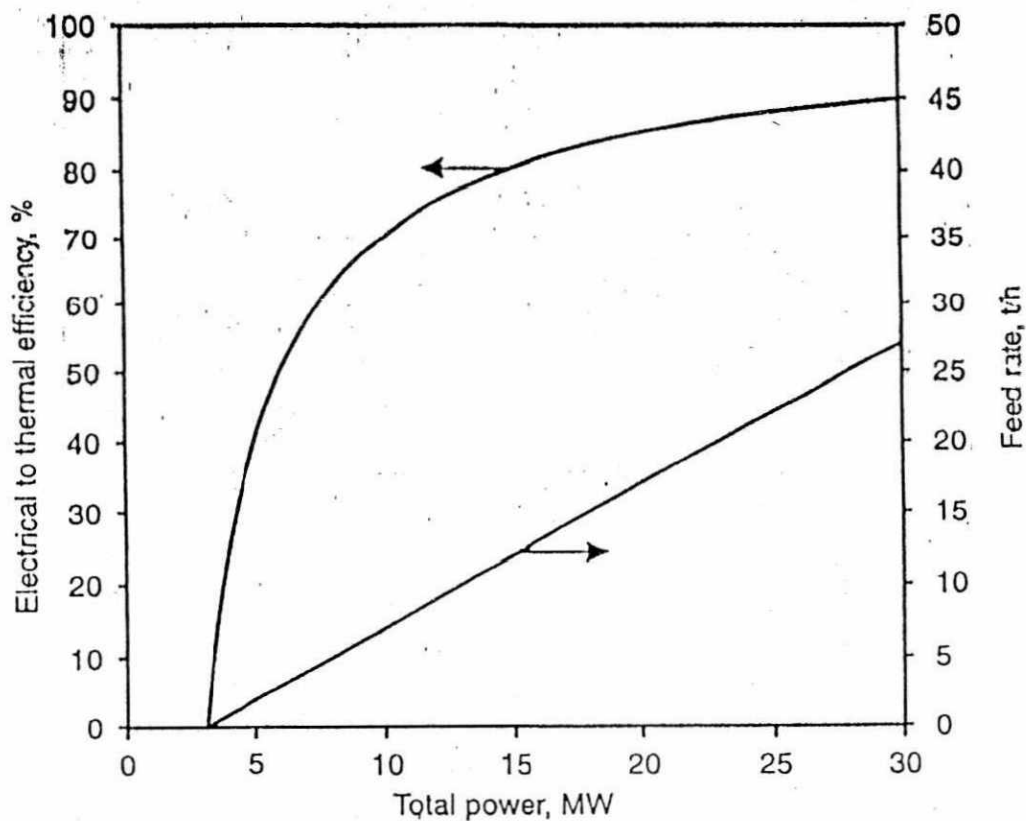


Fig.10 Efficiency relationship for a hypothetical 30 MW DC transferred arc furnace with a rate of loss of energy of 3 MW and operating on a process having an ideal energy requirement of 1 MWh/t [5]

Introduction

Synthetic slag practice is employed to obtain clean steels and to desulphurize molten steel. Synthetic slag practice is adopted to meet the following objectives

- i) To cover molten steel for cutting down heat losses.
- ii) To avoid reoxidation of steel from atmospheric oxygen because the molten steel transfer operations are done under atmospheric condition.
- iii) To remove inclusions from molten steel.
- iv) Using slag of desired basicity and sulphide capacity, deoxidized steel can be desulphurized to as low as 0.005%
- v) Synthetic slag practice is attractive due to low capital cost on equipment.

Desulphurization of steel

Synthetic slag practice can desulphurize steel up to 50% to 60% of original sulphur in steel.

The following properties are desirable in synthetic slag:

- i) Slag should have high sulphide capacity
- ii) Basic slag is required
- iii) Slag should be fluid to obtain faster reaction rates.
- iv) Slag should not cause excessive refractory wear.

For efficient desulphurization, steel should be deoxidized and slag carry-over should be minimized. Fireday ladles are not suitable if low sulphur steel is to be produced. Instead, dolomite or other basic refractory lined materials should be used. Argon bubbling is done.

Design of synthetic slag

The synthetic slag contains CaO, CaF₂, Al₂O₃ and with small amount of SiO₂. The principle component of synthetic slag is lime. Calcium fluoride increases the sulphide capacity of slag and helps fluidizing the slag. Often Al is present to deoxidize the molten steel since transfer of sulphur from molten steel to slag is followed by transfer of oxygen from slag to steel. Therefore deoxidation of steel is must for efficient desulphurization. Typically, slag contains 45 – 55%CaO, 10 – 20% CaF₂, 5 – 16% Al and 0 – 5%SiO₂. This slag is pre fused in solid state. Special synthetic slag can be designed for a specific purpose. For removal of oxide inclusions, a neutral slag with CaO/SiO₂ = 1 or 1.2 can be used, when no desulphurization is needed.

Issues related to synthetic slag practice.

Synthetic slag practice appears to be simple and not much capital investment is needed. Certain issues are:

- i. Desulphurization may vary from one heat to other if slag carry-over from BOF/EOF is not controlled. Oxygen content of steel should be same for consistent results.
- ii. CaO is the main component. It is hygroscopic and leads to hydrogen pick up
- iii. Argon bubbling is done to stir the bath. Temperature drop could be of the order of 10°C to 25°C for 150 – 250 ton heat. The temperature drop is resulting from radiation heat loss from surface and heat transfer due to argon bubbling.
- iv. The slag attacks the ladle refractory. Excessive amount of Ca F₂ results in refractory wear. Higher tap temperature increases refractory wear.

Alternative synthetic slag

A pre melted slag based on CaO and Al₂O₃ with small amount of Ca F₂ can alleviate the problem of refractory wear and hydrogen pick. Composition of CaO and Al₂O₃ can be selected so as to melt at 1400 – 1450°C. Small amount of Ca F₂ may be added. A synthetic slag consisting of 70%(50%CaO + 50% Al₂O₃), 25% CaO and 5% Ca F₂ could be used. This remelted slag, when used for desulphurization, has been found to reduce the problems associated with pre fused slag