

A PLASMA-ARC PROCESS FOR THE PRODUCTION OF MAGNESIUM

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SYNOPSIS

An investigation is reported in which magnesium was produced by a modified version of the industrial Magnetherm process, a plasma-arc system being used instead of the submerged-electrode furnace normally employed, and the reaction being carried out at atmospheric pressure instead of under vacuum.

The 50 and 100 kVA furnaces used in the tests are similar. Both furnaces employ direct current, and operate with a single graphite electrode as the cathode and the molten bath of process material as the anode. The raw materials constituting the charge were burnt dolomite (77 per cent), ferrosilicon (13 per cent), and alumina (10 per cent). The magnesium vapour produced in the furnace was recovered in a condenser-filter unit connected behind the furnace.

Based on slag analyses, the efficiency of extraction of magnesium was found to be about 85 per cent. Analysis of the crude condensed magnesium indicated that a product of high purity (99.8 per cent) is attainable by thermal reduction in a plasma-arc furnace. Operation at atmospheric pressure has the advantage that the process can be adapted easily to semi-continuous or continuous operation, and that the vaporization of manganese and silicon, which are relatively volatile, is suppressed. The levels of manganese and silicon in the crude magnesium produced

by the plasma-arc process were about 0.02 and 0.04 per cent respectively.

INTRODUCTION

Existing thermal processes for the extraction of magnesium are based on the silicothermic reduction of magnesium oxide. Ferrosilicon is normally employed as the source of silicon for the reduction of magnesium oxide in calcined dolomite. The Pidgeon process¹ involves the solid-state reduction of calcined dolomite by ferrosilicon in externally heated retorts at around 1150°C and in a vacuum of about 10 Pa. In the Magnetherm process², the heat is generated by resistance heating of a molten slag. Calcined dolomite is reduced by ferrosilicon in the presence of aluminium oxide. The addition of calcined bauxite or alumina lowers the melting temperature of the slag produced, and the reaction takes place in the liquid state at around 1550°C, and in a vacuum of about 5 kPa.

In the present work, a study was initiated on the production of magnesium by a modified version of the commercial Magnetherm process². A d.c. transferred plasma-arc furnace was used instead of the submerged-electrode furnace that is normally employed, and the reaction was carried out at atmospheric pressure instead of in a vacuum³. In theory, it is entirely possible to operate the magnesium-extraction process at atmospheric pressure.

Thermodynamic calculations predict that slags of similar compositions will be obtained (i.e. the extractions of magnesium in the furnace will not alter) irrespective of whether an inert gas (such as argon) or a vacuum is used, to achieve the same magnesium pressure in the furnace at the same operating temperature.

A transferred plasma-arc furnace is particularly useful for the thermal reduction of magnesium oxide because, the reaction zone cannot only be heated directly, but can achieve appropriately high temperatures, thus obviating the need for very low magnesium pressures in the furnace. The total pressure of the system, (comprising the partial pressures of the argon plasma gas and the magnesium vapour) is kept at atmospheric pressure. Operation at atmospheric pressure, besides requiring lower capital expenditure, has the advantages that vacuum-leakage problems and consequent reoxidation of the magnesium product are reduced, and that the process is more easily adapted to semi-continuous or continuous operation.

EXPERIMENTAL FURNACES AND OPERATING METHODS

Three series of tests - a 'combustion' series and two 'condensing' series - were conducted. In the first series of experiments, the magnesium produced was burnt to magnesium oxide and collected, as such, in a baffled settling chamber and a small bag filter. The second and third series of tests involved operation of the plasma furnace in combination with a condenser for magnesium metal instead of a combustion chamber. Two similar furnaces were employed: one of 50 kVA, the other of 100 kVA. The 50 kVA furnace was used for the combustion testwork and for the first series of condensing tests. The 100 kVA furnace was employed for the last group of condensing experiments.

The 50 kVA furnace with combustion chamber

The test equipment consisted of a transferred plasma-arc furnace, which has a 50 kVA direct-current power supply and a reaction

vessel with a production capacity of about 1 kg magnesium per hour. The furnace is shown in Figure 1, and comprises a graphite crucible, a steel shell, a single graphite electrode (cathode), a cylindrical copper-anode connection, a water-cooled combustion chamber (which also functions as a settling chamber), and a small bag filter. The assembly is made gas-tight by means of water-cooled flanges equipped with rubber sealing rings. The roof section has three apertures - a central entry port for the electrode, a feed port, and an off-gas duct. The cathode contains a central hole for the supply of plasma gas, its entry port being sealed from the atmosphere by means of a flexible stainless-steel bellow. The cathode is a composite electrode. The top section consists of water-cooled copper, and is attached to the bottom (graphite) section by means of a copper nipple. During operation, the graphite section is situated inside the furnace; the copper section projects through the roof inside the metal bellow. The feed system comprises two Monaci-type⁴ feeders and two sealed hoppers. Thermocouples are located at different positions in the refractory lining, the roof, the anode, the off-gas duct, the combustion chamber, and in the cooling-water inlet and outlet conduits.

At the start of each experiment, one of the feed hoppers was filled with a mixture of 3.2 kg of calcined dolomite and 0.4 kg of alumina, while the other feed hopper contained 0.55 kg of ferrosilicon. About 0.5 kg mild steel was placed on the hearth of the graphite crucible. During the first 60 minutes of the run, the power was gradually raised from 5 kW to about 40 kW. After this pre-heating period, feeding was commenced, a feed rate of 5 kg/h being maintained throughout the remainder of the experiment. The unit was operated at 60 V and 700 A, which provided for a power supply of approximately 40 kW. Air was delivered to the combustion chamber at a rate of 150 l/min. Argon was used as the plasma gas (6 l/min) and as the purging gas at a total flowrate of 20 l/min. The system was kept near to atmospheric pressure during the extraction process. The partial

pressure of magnesium was about 0.3 atm. At the end of the tests (a typical run lasted about 2 hours), the products inside the furnace and the combustion chamber were left to cool for about 24 hours, after which they were removed, weighed, sampled, and analysed.

The 50 kVA furnace with condenser

The test equipment shown in Figure 2 includes the same 50 kVA plasma furnace that was used in combination with the combustion chamber. The equipment differs from the arrangement previously described in that the combustion chamber has been replaced by a condenser. The condensing unit consists of two main parts - a vertical steel cylinder and a steel crucible to collect the magnesium. A second cylinder, also made of steel, is mounted round the condensation cylinder. A resistance (Cr-Ni wire) heating element rated at 3 kW is positioned between the two coaxial cylinders. Most of the remaining space between the two cylinders is packed with thermal insulation (ceramic-fibre blanket). The condenser is connected to the furnace via a water-cooled flange. The vapour leaves the furnace via a central pipe mounted at the top of the condenser. This pipe is connected to a dilute solution of hydrochloric acid, which provides a seal, and is further intended to catch uncondensed magnesium vapour and dust. Chromel-alumel (K-type) thermocouples are placed at different positions inside the condensing unit so that its temperature can be regulated and recorded.

The feed recipes and operating procedures employed were the same as those used previously for the 'combustion' tests. The flowrate of argon was varied so that the effect of the partial pressure of magnesium on the efficiency of magnesium extraction and condensation could be established. The total feed per batch test varied between 5 and 15 kg. The temperature inside the

condenser was maintained at above 650°C, the melting point of magnesium, which was sufficiently high to ensure that the magnesium vapour condensed as a liquid and flowed down to the collecting crucible under the condenser. On completion of an experiment, each of which ran for about 3 hours, the reactor-condenser unit was allowed to cool to room temperature before it was opened and the magnesium product was removed. In the course of the investigation, a slag tap-hole was installed to allow semi-continuous operation of the facility.

The 100 kVA furnace

This unit consists of a transferred plasma-arc furnace with a 100 kVA direct-current power supply, a sealed reaction vessel with a production capacity of about 3 kg of magnesium per hour, an externally heated (10 kW) condenser, a porous metal filter, and an air-tight feed system comprising two vibratory feeders and two feed hoppers. The general arrangement of this pilot plant for the production of magnesium is shown in Figure 3.

At the start of the tests, one of the two feed hoppers was filled with a mixture of calcined dolomite and alumina, while the other was filled with ferrosilicon. The formulation of the feed mixture was kept constant during the testwork at 77 per cent calcined dolomite by mass, 13 per cent ferrosilicon by mass, and 10 per cent alumina by mass. The feed hoppers were evacuated and flushed with argon at the start of an experiment, and after each re-fill during the testwork. Initially, a mixture of ferrosilicon (75 per cent silicon) and iron was used to establish a molten pool of ferrosilicon (containing about 20 per cent silicon) in the bottom of the reaction crucible.

During the first 60 minutes of the run, the power was gradually raised from 15 to 70 kW (700 to 900 A, 80 to 100 V). The charge was then fed at a rate of about 10 kg/h, which, over a period of 60 minutes, was increased to a normal operating feed rate of 25

kg/h. The furnace was tapped after each batch of 20 to 40 kg of calcined dolomite, alumina, and ferrosilicon had been fed to the furnace. The total flow of argon during the tests was kept at about 30 l/min, i.e. the argon plasma gas and the pure argon gas to the feed hoppers, the window, the condenser, and the space between the electrode and its flexible seal. At the end of each campaign, which consisted of 3 to 5 smelting-tapping operations, the reactor-condenser unit was allowed to cool. The condenser was then disconnected from the furnace, and the magnesium product was removed, weighed, and analysed.

CHEMICAL COMPOSITIONS OF FEED MATERIALS AND CONDENSED PRODUCTS

The chemical compositions of the feed materials used in the experiments are shown in Table I. The grade of the calcined dolomite used for the testwork in the 50 kVA furnace (calcined dolomite 1) was higher than that of the calcined dolomite employed for experiments in the 100 kVA furnace (calcined dolomite 2). The magnesium oxide content of calcined dolomite 1 was higher, and its silica, ferrous oxide, and manganous oxide contents were lower than those of calcined dolomite 2. The charges were always made up of fine materials (smaller than 6 mm in size). It was found convenient to lower the melting point of the slag with refractory-grade high-purity alumina instead of calcined bauxite or Bayer alumina, which is normally employed.

Table I Chemical compositions of raw materials

(All values are expressed as percentages by mass)

Material	MgO	CaO	SiO ₂	Al ₂ O ₃	FeO	MnO	L.O.I.
Calcined dolomite 1*	38.0	57.6	1.1	0.4	0.4	0.2	0.3
Calcined dolomite 2*	35.8	55.5	2.6	1.0	1.4	1.5	0.5
Alumina	-	0.1	0.1	99.3	0.4	-	-
Material	Si	Fe	Al	C	Ca	Mg	Mn
Ferrosilicon	75.5	18.1	2.4	0.1	0.7	0.03	0.1

* Calcined dolomites 1 and 2 were used for testwork on the 50 kVA and 100 kVA furnaces respectively.

L.O.I. Loss on ignition

Table II presents the chemical compositions of the condensed magnesia fumes produced in five smelting operations, in which the magnesium extracted in the furnace was subsequently burnt to magnesium oxide. A product with a magnesium oxide content of between 96 and 99 per cent was obtained, while the balance was composed mainly of calcium oxide (about 2 per cent) and silica (about 0.5 per cent). The chemical compositions of the magnesia fumes gave an initial estimate of the purity level of magnesium that is attainable by the silicothermic reduction of calcined dolomite in a plasma operation. Calcium and silicon, together with magnesium, are the main constituent metallic elements of the starting materials, and could therefore be expected to be the major impurities in the final product.

(ISO) specifications (ISO 114-1980) for the magnesium ingot are: magnesium a minimum of 99.8 per cent, calcium, silicon, aluminium, and iron each a maximum of 0.05 per cent, and Mn a maximum of 0.1 per cent.

Table III Chemical compositions of magnesium metal produced
(All values are expressed as percentages by mass)

Test no.*	Mg	Ca	Si	Al	Fe	Mn
1	99.59	0.22	0.05	0.04	0.08	0.02
2	99.64	0.07	0.06	0.04	0.18	0.01
3	99.82	0.09	0.02	0.02	0.02	0.04
4	99.83	0.10	0.02	0.01	0.02	0.02
5	99.74	0.16	0.03	0.03	0.03	0.01
6	99.76	0.12	0.07	0.02	0.01	0.02
\bar{x}^+	99.73	0.13	0.04	0.03	0.03	0.02
\bar{x}^*	99.68	0.12	0.03	0.02	0.02	0.11

* Tests 1 to 6 were conducted in the 50 kVA furnace

+ \bar{x} : Average composition of Mg metal produced in the 50 kVA furnace. (6 tests, standard deviation for percentage Mg: 0,10).

* \bar{x} : Average composition of Mg metal produced in the 100 kVA furnace. (8 tests, standard deviation for percentage Mg: 0,12).

It is evident from the above results that, with respect to calcium, silicon, and aluminium impurities, the plasma-arc process is capable of producing a crude magnesium that is superior in quality to that produced by the Magnetherm process⁵. Therefore operation at atmospheric pressure instead of under vacuum appears to have the advantage that undesirable side

Table II Chemical compositions of condensed magnesia fumes from the 50 kVA plasma furnace
(All values are expressed as percentages by mass)

Test no.	MgO	CaO	SiO ₂	Al ₂ O ₃	FeO	MnO
1	98.3	1.5	0.1	<0.1	<0.1	<0.1
2	96.1	2.0	1.4	0.2	<0.1	0.2
3	98.2	1.4	0.3	<0.1	<0.1	0.1
4	96.8	2.4	0.5	<0.1	<0.1	0.2
5	97.6	2.0	0.1	<0.1	<0.1	0.2

The chemical compositions of the magnesium metals produced in six smelting operations in the 50 kVA furnace with condenser are presented in Table III. The magnesium from these six tests contained, on average, the following impurities: 0.13 per cent calcium, 0.04 per cent silicon, 0.03 per cent aluminium, 0.03 per cent iron, and 0.02 per cent manganese. The average composition of the magnesium metal produced in the 100 kVA furnace (Table III), using a lower grade of calcined dolomite, was (except for the higher manganese content) similar to that obtained from the 50 kVA furnace. It is emphasized that the magnesium recovered from the condenser was not refined, as is the practice in industry, to produce a commercial product. Samples of unrefined or crude magnesium produced by the Magnetherm process have been analysed and shown to contain 0.77 to 1.05 per cent calcium, 0.11 to 0.16 per cent silicon, and 0.04 to 0.09 per cent aluminium⁵. Bowman⁵ found that about 70 per cent of the calcium and about 80 per cent of the silicon were present as metallic impurities dissolved in the magnesium; aluminium was present predominantly as non-metallic inclusions. Refining with a salt flux (KCl-MgCl₂ mixture) successfully produces magnesium of commercial purity from the crude magnesium manufactured by the Magnetherm process. The International Organization for Standardization

reactions (the formation of silicon monoxide, calcium, and manganese vapour) are suppressed, and that possibly, less feed is carried over from the furnace to the condenser. Consequently, less salt flux will be required for the refining of the crude magnesium, and it may be possible to produce a magnesium ingot of higher purity from the crude magnesium produced in the plasma-arc furnace.

EFFICIENCY OF MAGNESIUM EXTRACTION AND CONDENSATION

The percentage magnesium extraction was defined as follows:

$$\% \text{ Mg extraction} = \frac{\text{Mg in feed (kg)} - \text{Mg in slag (kg)}}{\text{Mg in feed (kg)}} \times 100.$$

The chemical compositions of the slags obtained during the production of magnesia fume and magnesium metal are given in Tables IV and V respectively. A typical Magnetherm slag contains 6 per cent magnesium oxide, 55 per cent calcium oxide, 25 per cent silica, and 14 per cent alumina. The slags produced during the testwork were of similar composition. The magnesium extractions calculated according to the above formula are also presented in Tables IV and V. The average magnesium extraction was 84 per cent, which is about the same as that obtained in the

commercial Magnetherm process.

Table IV Chemical compositions of slags produced during magnesium 'combustion' testwork in the 50 kVA plasma furnace

Test no.	Constituent, % (by mass)				Mg extraction* %
	MgO	CaO	SiO ₂	Al ₂ O ₃	
1	4.3	55.7	26.6	13.0	88
2	4.2	56.7	24.2	14.6	90
3	5.9	56.4	23.3	12.5	84
4	4.5	56.3	23.7	14.5	87
5	4.8	56.0	24.1	14.6	87

* % Mg extraction = (Mg in feed - Mg in slag)/Mg in feed x 100

Table V Chemical compositions of slags produced during magnesium 'condensing' testwork on the 50 kVA plasma furnace

Test no.	Constituent, % (by mass)				Mg extraction*
	MgO	CaO	SiO ₂	Al ₂ O ₃	
1	6.2	56.0	24,2	13.6	82
2	6.0	56.7	23,3	13.6	82
3	4.7	56.2	22,3	12.9	89
4	7.0	54.3	25,0	9.9	77
5	6.3	47.7	31,9	10.8	83
6	7.4	54.4	23,8	11.2	80

* % Mg extraction = (Mg in feed - Mg in slag)/Mg in feed x 100

In Figure 4, the efficiency of the condenser is shown as a function of the partial pressure of magnesium in the furnace. The efficiency of the condenser was calculated as follows:

% condenser efficiency =

$$\frac{\text{Mg recovered from the condenser, (kg)}}{\text{Mg vapour produced, (kg)}} \times 100,$$

where Mg vapour is defined as Mg in feed (kg) - Mg in slag (kg).

The partial pressure of magnesium in the furnace was derived from the argon flowrate and the rate of evolution of magnesium vapour. The rate of evolution of magnesium was calculated from the amounts of magnesium fed and magnesium left in the slag, and from the duration of the test, according to the following formula:

$$\text{Rate of magnesium production} = \frac{\text{Mg in feed (kg)} - \text{Mg in slag (kg)}}{\text{feed time (min)}}$$

The total pressure inside the system, including the partial pressures of both the magnesium and argon, was kept near atmospheric pressure ($P_{\text{Mg}} + P_{\text{Ar}} = 1 \text{ atm}$). The efficiency of the condenser increased with increasing partial pressure of magnesium in the furnace, and therefore also with increasing partial pressure of magnesium in the vapour entering the condenser. Avery⁶ claims that, when an inert gas is used in the production of magnesium, the efficiency of condensation is substantially increased when the transport of magnesium is predominantly by diffusion and not so much by the sweeping action of the inert gas. The flowrate of the magnesium vapour to the condenser should be equal to or greater than that of the inert gas, rather than the other way about.

The relation that was established in the present investigation between the efficiency of the condenser and the partial pressure of magnesium (Fig. 4) is in accordance with the above findings.

A magnesium partial pressure of 0.5 atm was about the highest that could be attained on the relatively small scale of operation. The reason for this was that at least 10 litres of argon per minute was required to stabilize the plasma arc, while the maximum rate of magnesium production was about 3 kg/h. An industrial-size plasma-arc furnace would allow more flexibility regarding the selection of the magnesium partial pressure, because less argon per kilogram of product would be required to stabilize the plasma arc.

With regard to the extraction process, a decrease in the partial pressure of magnesium in the furnace is associated with a lowering of the free-energy change in the magnesium-producing reaction and, hence, a reduction in the temperature at which the reaction becomes possible. This is demonstrated in Figure 5 where the standard free-energy change of the reaction $2(\text{CaO.MgO}) + \text{Si} \rightarrow 2\text{Mg} + 2\text{CaO.SiO}_2$ is shown as a function of temperature. Lines of different magnesium pressures are also plotted in this diagram, and their intersections with the reaction line provide the minimum reaction temperatures at different magnesium pressures. In the present investigation, no relation was found to exist between the percentage magnesium extraction and the partial pressure of magnesium in the furnace. Therefore, variations in the partial pressure of magnesium in the range of operation ($P_{\text{Mg}} = 0.3$ to 0.5 atm) did not noticeably affect the extraction, although the minimum reaction temperature is rather

sensitive to these changes in magnesium pressure changes.

CONCLUSIONS

A novel plasma-arc process for the production of magnesium has been successfully demonstrated on the 50 kVA and 100 kVA scales of operation. The 100 kVA furnace was operated at 70 kW (800 A, 90 V), with a delivery rate of 25 kg of feed material per hour, which provides for a production capacity of about 3 kg of magnesium per hour. The reaction was carried out at atmospheric pressure, argon was used as the plasma gas, and the charge consisted of calcined dolomite, ferrosilicon, and alumina. High-purity products having magnesium contents of around 99.7 per cent were obtained. The main impurity was calcium (about 0.1 per cent), which is readily removed in the conventional salt-refining step. It was possible to extract about 85 per cent of the magnesium from the feed material (calcined dolomite), and to condense about 70 per cent of the extracted magnesium at relatively high pressures of magnesium vapour in the furnace (about 0.5 atm). This provided for an overall recovery of magnesium (extraction and condensation) of about 60 per cent. Variations in the partial pressure of magnesium in the range tested (0.3 to 0.5 atm), did not appear to affect the efficiency

of the magnesium-extraction process in the furnace. An increase in the partial pressure of magnesium favoured the condensation of magnesium.

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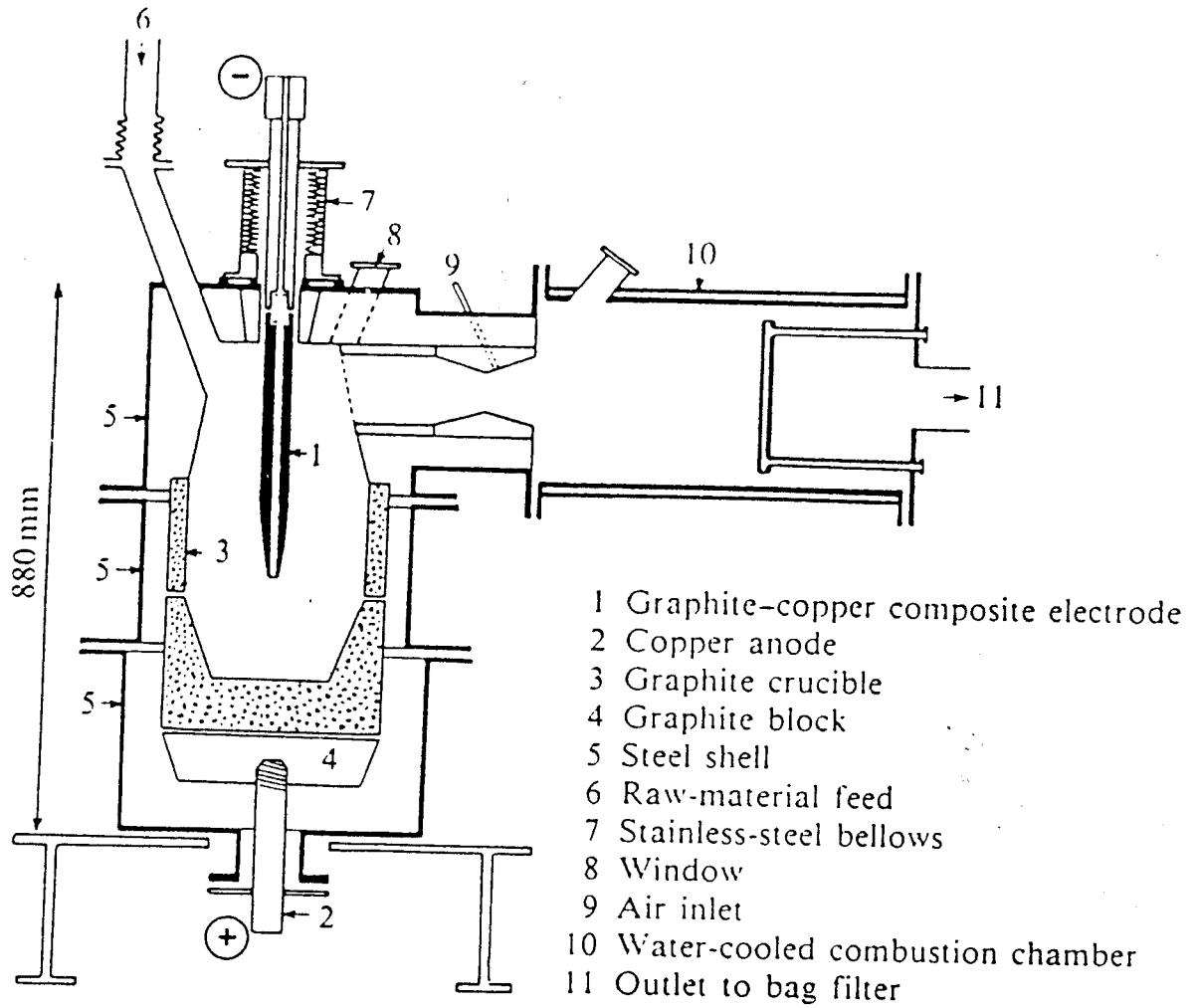
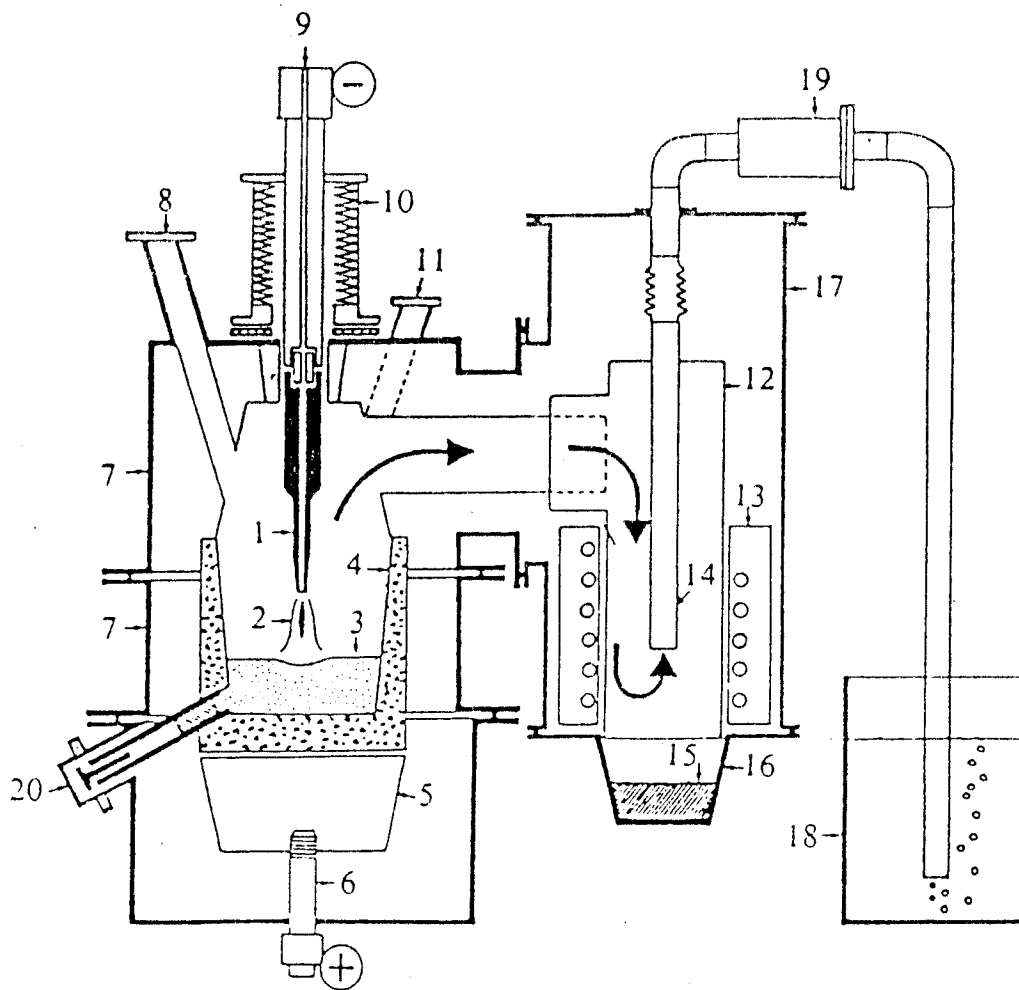


Fig. 1. The 50 kVA furnace with combustion chamber



- | | |
|---------------------------------------|--------------------------------------|
| 1 Graphite-copper composite electrode | 11 Window |
| 2 Plasma zone | 12 Inner cylinder of condenser |
| 3 Molten bath | 13 Kanthal wire heating element |
| 4 Reaction crucible | 14 Outlet pipe of condenser |
| 5 Graphite block | 15 Condensed magnesium |
| 6 Copper anode | 16 Condenser crucible |
| 7 Steel shell of furnace | 17 Outer shell of condenser |
| 8 Feed port | 18 Tank for dilute hydrochloric acid |
| 9 Supply of argon plasma gas | 19 Filter |
| 10 Steel bellows | 20 Taphole |

Fig. 2 The 50kVA furnace with condenser

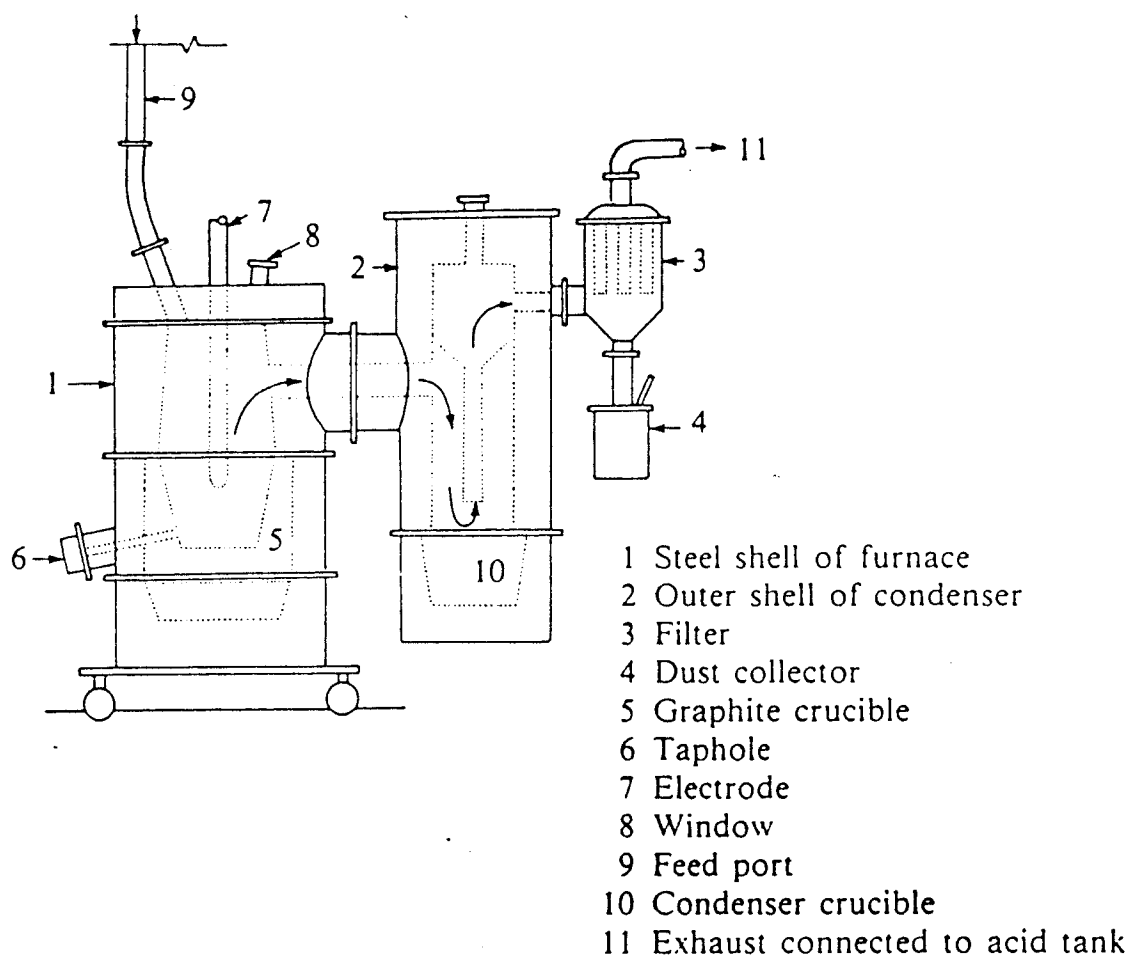


Fig. 3. The 100 kVA furnace with condenser

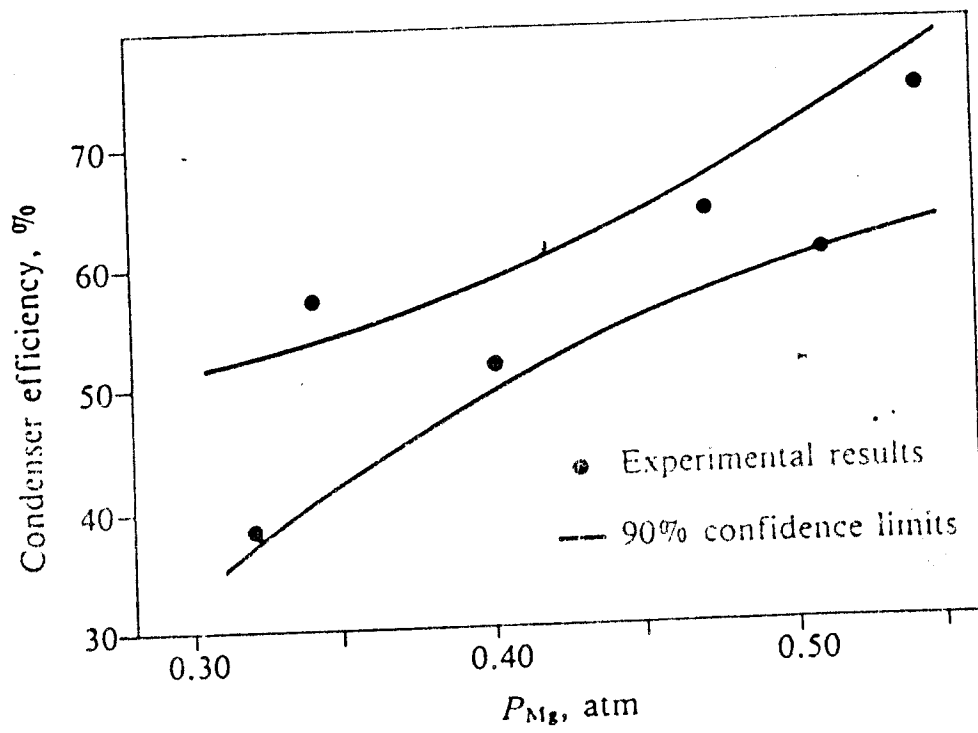


Fig. 4. The condenser efficiency as a function of the partial pressure of magnesium in the furnace

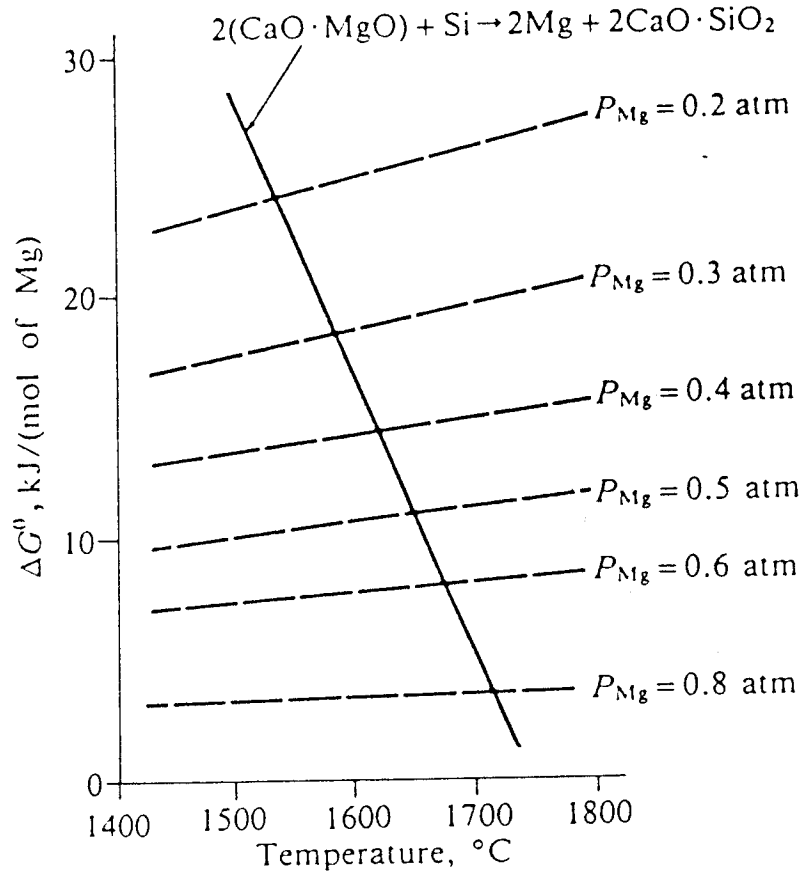


Fig. 5. Standard free-energy change (ΔG^0) as a function of temperature for the reaction $2(\text{CaO} \cdot \text{MgO}) + \text{Si} \rightarrow 2\text{Mg} + 2\text{CaO} \cdot \text{SiO}_2$ (after Barin and Knacke)

