THE SCOPE FOR DEVELOPMENT OF MAGNESIUM INDUSTRY IN INDIA

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IN THIS era of "sputniks" and "space flights", weight saving poses to be a problem of prime importance with its direct influence over increasing speed and fuel economy. Magnesium and magnesium base alloys are known to be the lightest structural materials today, and have been employed not only for space research and rocketry but for various types of aero, marine and road transportation vehicles.

The low density of magnesium combined with good machinability, damping capacity, rigidity without weight penalty, wearing qualities, heat and electrical conductivity and chemical resistance have rendered it eminently suitable for its multifarious applications. It can be subjected to sand or die-casting, rolling, simple or impact extrusion, forging, drawing, spinning, joining by welding, brazing, bolting or revetting and other standard processes necessary for an excellent engineering metal.

As a light structural, magnesium has found extensive applications in the field of missiles, air-craft landing wheels, reciprocating aero engines, wings, fuselage, manufacture of commercial high way transportation vehicles, industrial machinery tools, material handling equipment, packaging, foundry, printing, graphic arts, and for various military purposes such as construction of radar equipment, radios and accessories, tents, portable alert shelters, sleds, conveyors, shipping pallets, instrument cases and endless varieties of similiar items that must be carried by air. Besides the uses of magnesium as alloying element, deoxidiser and desulphuriser, it has been widely used for the reduction of halides and oxides for the production of newer metals like titanium, zirconium, uranium, etc. Magnesium powder is used in pyrotechnics. The principal chemical and electro-chemical uses of metallic magnesium include cathodic protection of underground pipelines, construction of batteries, and preparation of Grignard reagents for synthetic organic chemistry. The endwise application of magnesium in U.S.A. excluding export during 1956 was 31% for structural and 63·9% for non-structural purposes[1].

Increasing demand for magnesium created by its indispensable nature for wide range of applications is responsible for the phenomenal rise in its production from a meagre 10 lb in 1900 to a peak value of 238,500 tons in 1943 and the present world production is estimated at 0·15 million tons. Consequent to its large scale production and advancement in the knowledge of magnesium production, the price per pound of magnesium has dropped down from $5·00 in 1915 to 36 cents in U.S.A.

The principal magnesium producing countries are U.S.A., U.S.S.R., Germany, U.K., France, Canada, Norway and Italy. India's requirements of magnesium either as virgin metal or as finished product is met by imports alone. In the country's programme for self-sufficiency in the basic materials and the expansion of aircraft industries, the demand for magnesium is bound to increase manifolds and it is essential that serious efforts should, therefore, be made for taking up the production of magnesium in the near future.

Raw materials and resources

The chief minerals of commercial importance for extraction of magnesium are dolomite, magnesite, brucite and carnallite. India has vast resources of magnesium both as sea-water and as high grade mineral deposits. Dolomite or dolomitic limestone deposits have been found in Orissa, Bengal, Bihar, Maharashtra, Madhya Pradesh, Madras, Mysore, Punjab, Rajasthan, Uttar Pradesh, Jammu and Kashmir. The best known occurrences are in Birmitrapur area of Gangpur, Orissa and extend over a distance of more than 60 miles containing an estimated reserve of over 252 million tons[2,3]. Besides the high grade dolomites, certain low grade siliceous dolomites of Kashmir[4] and other parts in the Himalayan range containing about 6% impurities are also suitable for extraction purposes. Extensive

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deposits of magnesite have also been located at various places in India and the Salem deposits in Madras are the most promising both for purity and the reserves.

General methods of extraction

Though magnesium was first isolated in 1808, the production of the metal, based on fused salt electrolysis, started in 1886 and the industry grew with remarkable rapidity during the First World War. At the outbreak of Second World War, great enthusiasm for production of magnesium was supplemented by development of direct reduction processes, and magnesium is produced today by both electrolytic and direct reduction processes.

Electrolytic process: The electrolytic processes as practised at different plants are essentially similar except in the cell characteristics, and the use of magnesium chloride with different degrees of dehydration. Use of magnesium oxide in a fluoride bath similar to production of aluminium was not commercially attractive, when compared to the chloride process. Magnesium chloride used for electrolysis is prepared either by dehydration of the hexa-hydrate or direct production of anhydrous salt by chlorination of magnesium oxide in presence of carbon. The dehydration of magnesium chloride hexa-hydrate by heating requires rigid control owing to its tendency for decomposition to the oxide and hydrochloric acid. In the Dow Chemical process, the operation is carried out in two stages; first by converting it to tetra-hydrate and subsequently with dehydration to an indefinite compound containing 1·25 molecules of water, which is used as a cell feed. The dry chlorination process has been followed by several producers including the Pioneer German firm—I. G. Farben-industries. Principal differences in cell characteristics lie in the fact that in one case a steel pot with external heating arrangement is employed, whereas the other makes use of a refractory lined cell without any external heating source. Power consumption in both the cases ranges between 8·5–9 kWh per pound of magnesium.

Direct reduction: Earlier attempts for the direct reduction of magnesium oxide did not bear fruit on account of the high affinity of metal for oxygen. The chief difficulty encountered for the direct reduction of MgO was the difficulty of attaining the desired temperature for reaction or evolving means to remove one of the reaction products to enable the reaction to go to completion. The reduction of MgO by carbon may be represented as:

$$MgO + C = CO + Mg\,(g)$$

It was shown by Slade[5] that carbon can be used as a reducing agent if a reaction temperature of the order of 1,900°C is attained. The reverse reaction of Mg with CO forming MgO and C prevented the successful exploitation of carbon reduction till Hansgirg[6] developed a successful method for shock-cooling, the reaction product thus preventing the re-formation of MgO. The shock-cooling prevented the reverse reaction, but resulted in the formation of sub-microscopic particles of pyrophoric magnesium that required careful melting. The powder, however, could be suitably treated in vacuum or under an inert gas to yield magnesium in an aggregate form. Carbothermic process was first attempted by Hansgirg and units were later set up in Korea and in U.S.A. at Permanente, California[7].

The reducing agents used for direct reduction with formation of non-volatile oxide include calcium carbide, aluminium, aluminium-silicon alloy, iron-aluminium-silicon alloys, calcium silicide, ferro-silicon and metallic sodium. The ferro-silicon reduction process developed in Canada by Pidgeon is of outstanding commercial importance, and has been employed at several places. The reduction of dolomite by ferro-silicon is represented as:

$$2(CaO.MgO) + (Fe).\quad Si = (CaO)_2SiO_2 + 2Mg + (Fe)$$

The presence of lime in the dolomite is beneficial as it combines with silica as soon as it is formed, thus considerably decreasing the activity of silica in the reaction mixture. The continuous removal of magnesium from the reaction zone at the operating temperature and pressure shifts the equilibrium to the right and the reaction goes to completion. The kinetics of reaction are thus governed by the rate of removal of magnesium either by vacuum technique or use of an inert carrier gas. Reaction in a continuously moving stream of hydrogen has proved to be hazardous while use of argon or helium is prohibitive on economic grounds. The present commercial practice is to carry the reactions under vacuum. This has been possible owing to advances in vacuum technology and today silicothermal process is gaining ground. Availability of proper equipment and a fund of know-how evolved the possibility of producing thousands of pounds of magnesium per day at low pressures.

In Pidgeon's process, the reduction of briquetted calcined dolomite with ferro-silicon is carried out in heat resisting retorts at 1150°C under a vacuum of 0·1 mm Hg. The use of ferro-silicon as reducing agent is preferred as it grinds readily. Flourspar has been used as a catalyst and it has been observed to hasten the reaction. Both dry and wet practices have been followed for briquetting the mixture. Wet process offers comparative ease in briquetting, but an additional drying step is required before the briquettes are charged into retorts. The use of molasses or a suitable oil for binder has also been suggested.

The proper heat distribution in the retort charge is one of the chief requisites of the process and this has limited the retort dimensions in the Pidgeon's process. Amongst the various silico-thermal processes for the production of magnesium either independently developed or modified after the Pidgeon's process may be mentioned the internal heating used by Pistor[8] in Germany and Bagley in U.S.A.

A recent development in the silico-thermal reduction of dolomite has been the "Magnetherm process"[9] developed and patented by Le Magnesium Thermique Magnetherm, France.

The process consists of electro-thermal reduction of dolomite with a metallic reducing agent under vacuum in the middle of a liquid slag composed of lime, silica and alumina. Lumps of calcined or sintered dolomite,

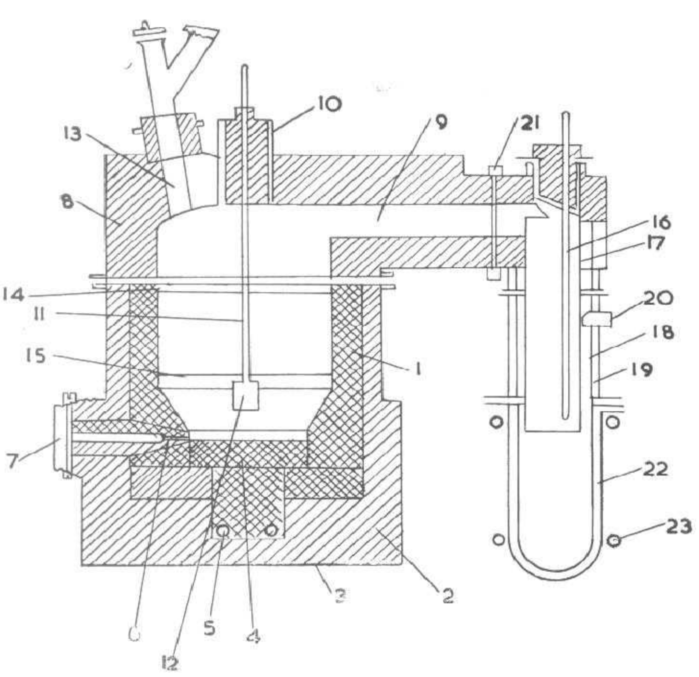

Fig. 1. A sketch of the Magnetherm Reactor.

1. Carbon lining. 2. Refractory insulation. 3. Steel shell. 4. Carbon bottom. 5. Current supply. 6. Tap hole. 7. Tap hole cover. 8. Insulation. 9. Vapour passage. 10. Electrode passage. 11. Electrode. 12. Electrode sleeve. 13. Hoppers. 14. Maximum slag level. 15. Minimum slag level. 16. Heater. 17. & 18. Steel flanges. 19. Condenser wall. 20. Vacuum pipe. 21. Flange. 22. Crucible. 23. Cooling tube

ferrosilicon containing over 70% silicon and aluminium oxide are charged in succession into the furnace. The reaction mass and slag are heated in the furnace by the current flowing through the graphite electrode and the carbon lined hearth that serves as the other electrode. The furnace roof embodies three hoppers through which raw materials are fed into the furnace via automatic tight-fitting valves. Proper slag level is maintained by periodically tapping out the slag. Magnesium vapour is led to the condenser where it condenses as liquid metal and trickles down to the cooled crucible for solidification. An efficiency of 85% has been claimed. A sketch of the Magnetherm Reactor is shown in Fig. 1.

Serious efforts are being made in making the silico-thermal process a continuous one and a number of modifications of introducing the reactants have been patented[10],[11]. There is no doubt that the continuous process shows good promise and in times to come, the future expansions will be on the continuous silico-thermal processes.

Though a substantial quantity of magnesium is being produced in the already existing electrolytic plants, the recent trends in the installation of new units clearly indicate a preference for the silico-thermal processes. The direct reduction of dolomite has found wider applications on account of the simplicity of the process, less power requirements, flexibility to meet increasing demands and, above all, the purity and price of the metal produced.

Recent trends and present status of magnesium metallurgy

For reduction of dolomite based on Pidgeon's process, a major power requirement can be met in the form of heat generated by combustion of fuels and it is not necessary that cheap electric power should be available at the site whereas the availability of cheap electric power is a pre-requisite for the electrolytic process.

The reasons for the supply of major requirements of magnesium by electrolytic process may be attributed to the existence of already well established plants with their inherent advantages. It may, for example, be noted that the 75% requirements of magnesium outside the Communist block are met from the production in U.S.A. with Dow-Chemical and its subsidiaries contributing a major share. The Dow-Chemical, one of the largest producers since the time when silico-thermal process was not even thought of, have some of the natural advantages without which it would not be able to compete with the much cheaper processes now being developed. Amongst the natural advantages may be mentioned the availability of unlimited supply of natural gas providing heat and electric power at low cost and an inexhaustible supply of sea water and the purest form of lime in proximity. Besides these, the plants were erected at a period when the cost of capital equipment and erection was very low. It is therefore justifiable that the world trend towards magnesium production should be viewed only in the light of new plants being set up and by 1952, the silico-thermal process was at par with the electrolytic processes. Ball[8], in his presidential address to the Institute of Metals in London emphasised the advantages of the silico-thermal processes and indicated that the mounting cost of electric power has been deterrent to the electrolytic production of magnesium. The cost of electric power in U.K. has gone up five-folds the pre-war level and it has now become impossible to operate the established electrolytic factories without the Government subsidy. Increasing attention is, therefore, being paid to do away with the electric power by establishing plants based on silico-thermal processes.

In France, the mounting cost of electricity since war greatly affected the economy of electrolytic process. Tentative research activities have led to the development of the silico-thermal process like the "Magnetherm process" on a commercial scale. A plant[12] has been erected at Beaudean (Hautes-Pyrenees) producing 50 tons of metal per month.

American interest in direct reduction processes during the early days of development of these processes is seen from gradually increasing production figures from 1942 onwards, as recorded in Table I.

The Dominion Magnesium Co. is one of the major magnesium producers in Canada. Technical developments in the silico-thermal process, adopted in the plant, have increased the plant efficiency by 60% above its original capacity. The company has entered into an agreement with Brooks and Perkins Inc., Detroit for construction of a silico-thermic reduction plant at Selma.

TABLE I
Production trends in U.S.A.

Year	Per cent production by Electrolytic	Carbothermic	Silicothermic
1942	94	2	4
1943	85	4	11
1944	81	5	14
1945	91	0	9
1952	77	0	23

From the information available[13], it is learnt that Russia is also developing the silico-thermal process, which appears to resemble the "Magnetherm" process.

Italian production is entirely based on silico-thermal reduction process. The Samis Aosta Co. has been producing the metal since 1945 with an annual capacity of 4,000 tons.

Germany tried to develop suitable direct reduction processes to replace the electrolytic process. I.G. Farben-Industries is one among such enthusiastic concerns. A commercial electro-thermic plant has been installed near Cologne in West Germany. Annual production of 15,000 tons by 1960 was under plan in 1956[14]. Currently a continuous thermal reduction process is being developed and attempts are being made to put up larger plants[12].

Magnesium production in Japan was mainly dependent on sea water. The production, ceased at the end of war, has been restarted by Riken Kinzoyu Co. at Ube, and operates on I. G. electrolytic process. It has been reported that recently the Ashai Chemical Products Co. has entered into an agreement with Pechiney to establish a direct reduction plant utilising sea water. The proposed plant will have an annual output of 2,000 tons of metal. The cost of production by silico-thermic process is reported[15] to be between 250,000 to 260,000 Yen as compared to 305,000 Yen by other methods.

As indicated above, a gradual diversion of thoughts of the magnesium producing concerns from electrolytic to direct reduction processes is a proof of the sound economic proposition of the latter process and there is no doubt that in no distant future the bulk production of magnesium will be by silico-thermal process.

Studies undertaken at the National Metallurgical Laboratory

In view of the obvious advantages of the silico-thermal reduction process and the increasing interest that is evinced of late, systematic studies have been undertaken at the National Metallurgical Laboratory for working out the details utilising indigenous raw materials. A sample of dolomite containing 22·85% MgO, 29·14% CaO, 2·15% SiO_2 and 45% L. O. I. was used during the investigation and solid state reduction under vacuum was studied. Laboratory scale experiments have been carried out for studying several factors such as temperature of reduction, effect of insolubles, degree of comminution of reactants, influence of briquetting pressure, effect of addition of various catalysts on kinetics of the process, and condensation characteristics of the magnesium vapour, etc.

The vacuum set-up for the studies consisted of a horizontal tubular furnace with a non-porous refractory tube of 2″ dia, a mechanical oil sealed rotary vacuum pump, vacuum gauge and accessories. Briquettes made from calcined powdered dolomite, ferro-silicon and a suitable catalyst were used for the experiments. It was observed that the dry mixture had good briquetting properties and the use of either a binding agent or water was not required. To study the recovery and reaction kinetics, an arrangement for introducing and withdrawing the briquettes contained in a nickel crucible without breaking the vacuum, was incorporated. Briquettes were drawn into the hot zone under vacuum as soon as the desired constant temperature was attained in the furnace and at the end of the reaction time, the sample was again withdrawn into the cooler zone of the tube without disturbing the vacuum. A series of experiments were carried out for two-hour periods at a pressure of 0·1 mm Hg varying the temperature of reaction and the results are indicated in Fig. 2.

It has been observed that the percentage recovery of magnesium shows a steep rise from 1000°C to 1080°C and thereafter remains almost steady. During the above experiments, magnesium vapours were condensed on a hollow cylindrical condenser closed at one end with a perforated disc, placed inside the refractory tube at its cooler end, facing the open end of the nickel container. Experiments were carried out to study the nature of magnesium condensate deposited at different temperatures. A cylindrical split type of

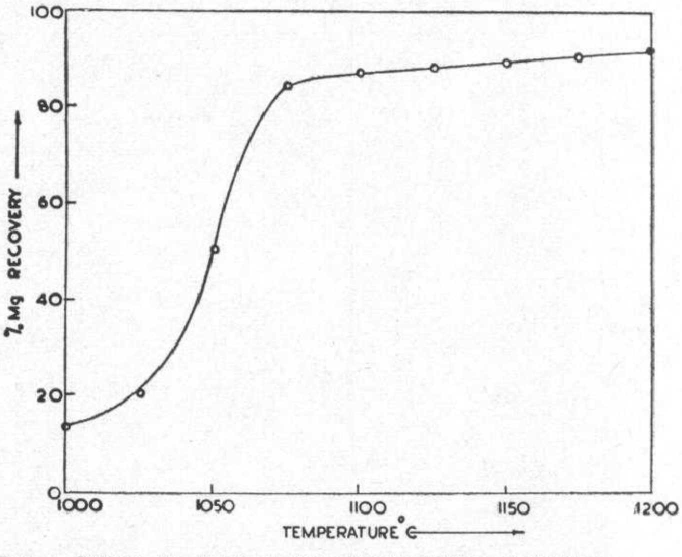

Fig2 EFFECT OF TEMPERATURE ON MAGNESIUM RECOVERY

Fig. 2.
Effect of temperature on magnesium recovery.

condenser with a lip tightly fitting the refractory tube was made. Stainless steel discs with perforations on one half of the discs were supported at the middle of the split condenser by passing the discs through a threaded hollow stainless steel tube. The threads helped in placing the discs at desired distances from one another. The whole condenser arrangement was placed inside the refractory tube in such a position that one end of it recorded a temperature around 800°C while the other end remained at about 200°C. A thermocouple placed inside the threaded hollow stainless steel tube helped in recording temperature around the discs distributed over the whole length of the condenser. It was observed that there was no deposit of magnesium on the discs recording temperatures from 800 to 530°C. Coarse deposits of magnesium were found on the discs lying around the temperature zone of 530 and 400°C. Finer deposits were noticed along the zone below 400°C and the metal deposited at lower temperatures was pyrophoric.

The reactions to study the effect of briquetting pressure on the percentage recovery of magnesium were carried out at 1100°C for 2 hours at a pressure of 0·1 mm Hg. The percentage recovery is indicated in Fig. 3 and it is observed that the recovery of magnesium increases rapidly from 52% without briquetting, to 72% at 1,000 p. s. i. and thereafter gradually increases to a maximum recovery of 84% at and beyond 3,000 p. s. i. The higher recoveries due to denser briquettes can be attributed to the greater proximity with better surface contact of the reactants. The heat penetration is also better with closer packing of the reactants.

Experiments were also carried out to study the reaction kinetics. The reactions were carried out up to 3 hours at 1,100°C at a pressure of 0·1 mm Hg. It is observed that the magnesium recovery increases rapidly from 15 mins. to 90 mins., and then shows no appreciable change. The percentage recoveries are indicated in Fig. 4.

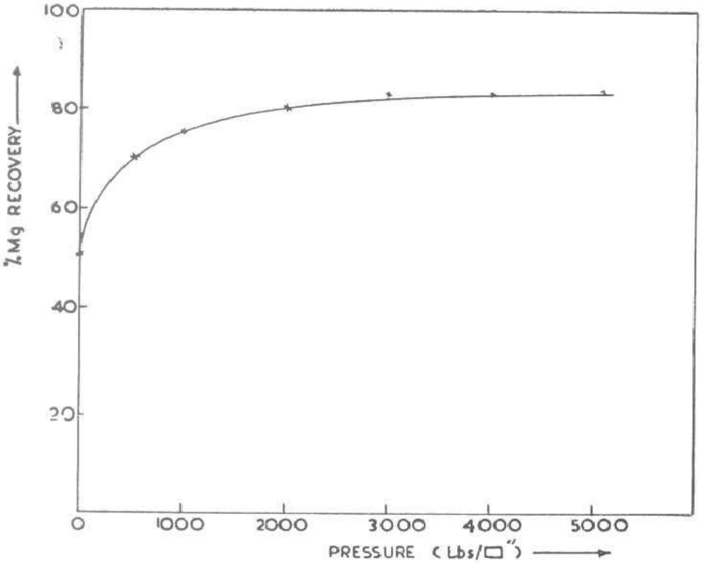

Fig. 3.

Effect of briquetting pressure on recovery of magnesium.

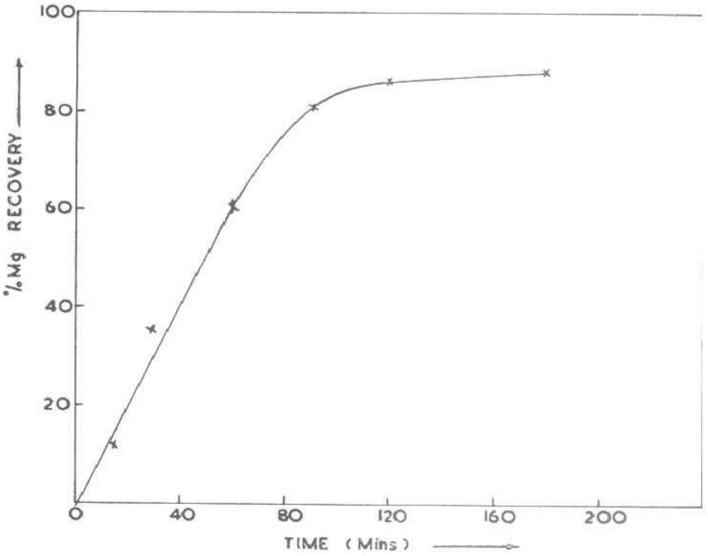

Fig. 4.

Effect of period of reaction on magnesium recovery at 1100°C.

Further studies have also been made to investigate the effect of particle size of reactants, grade of ferrosilicon, addition of catalysts and their reaction kinetics, pressure in the system on magnesium recovery and the nature of condensate, etc. The exact findings will be published elsewhere.

On the basis of laboratory scale studies, larger experimental units were designed and fabricated. Initially an internally heated vacuum furnace was employed where the crucible was made of a refractory material but was abandoned due to refractory failure. Later on, the reduction was carried out in a heat resisting alloy retort. The experimental retort was 6 in. in diameter and produced one pound of magnesium per batch. The retort as well as a suitable condenser unit were fabricated in the laboratory. The condenser assembly was made so as to facilitate separate condensation of alkali metals which are also reduced during the conditions of reaction. Experiments have shown that this separation is necessary for obtaining a good pure metallic condensate. That portion of the condenser containing the alkali condensate is detached first and collected under kerosene oil. This arrangement eliminated the chance of oxidation of a part or whole of the magnesium deposit due to extension of possible fire that sometimes originates from the alkali deposit. Proper positioning of a set of baffles inside the retort helped in attaining a desired temperature in the condenser zone. A temperature between 450 and 500°C results in obtaining a bright massive deposit of magnesium crystals. The reactions were carried out under a vacuum of about 0·05 mm Hg using an oil sealed rotary pump for evacuating the system. The general assembly using the 6″ dia. retort is shown in

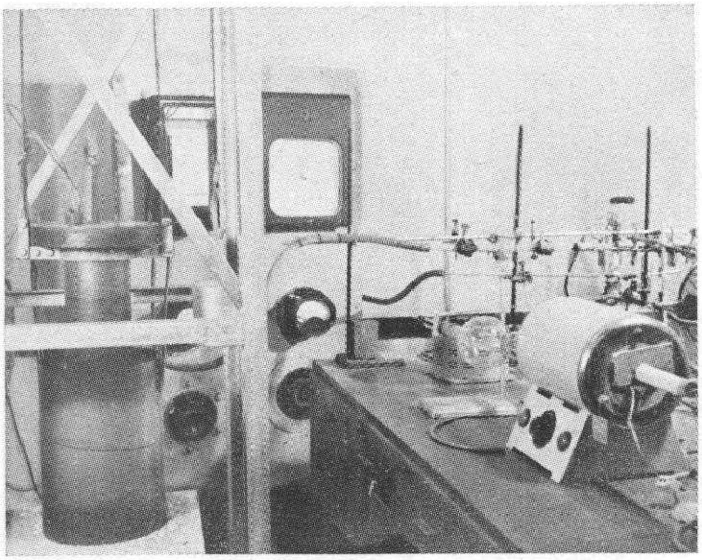

Fig. 5.
An assembly with the 6″ diameter vacuum retort.

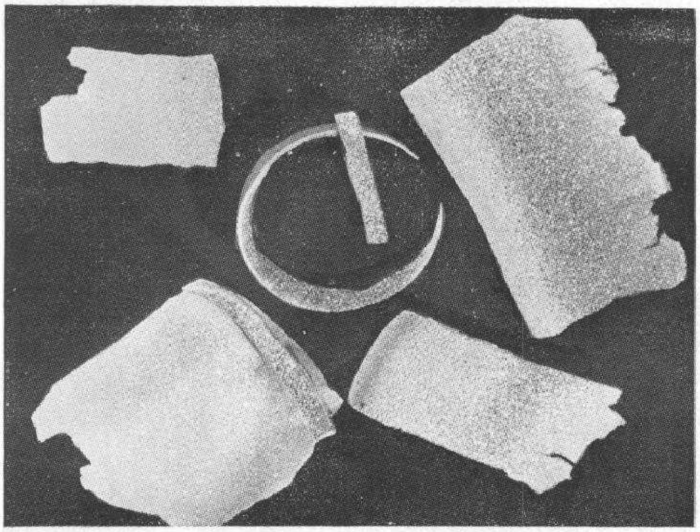

Fig. 6.
Magnesium deposits collected from the condenser.

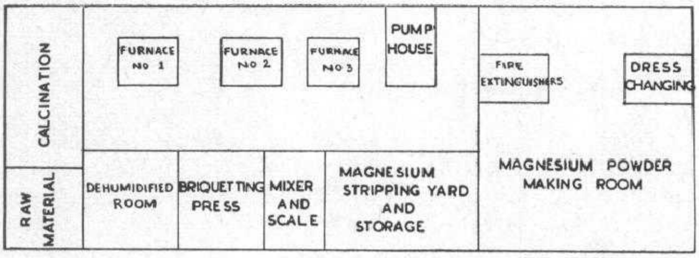

Fig. 7.
A layout of proposed magnesium pilot plant.
Area = 80′×30′ = 2400 sq ft.

Fig. 5. The analysis of the deposited metal is shown in Table II. The nature of deposit is shown in Fig. 6.

TABLE II
Chemical analysis of magnesium metal.

Cadmium	Traces
Manganese	0·025%
Copper	0·002%
Aluminium	0·002%
Zinc	0·003%
Iron	Not detected
Magnesium	Remainder

The one pound unit now in operation has greatly helped the authors in designing a pilot plant for producing 25 pounds of magnesium metal per day.

Attempts were also made to produce magnesium powder having various bulk densities to the specification of defence requirements and the results have been encouraging. It is also proposed to incorporate a powder-making unit in the pilot plant. A layout of the proposed plant covering an area of 2,400 sq ft is indicated in Fig. 7.

The successful operation of the envisaged pilot plant would no doubt go a long way towards establishment of industrial units in the country to meet the ever-increasing demands for the metal.

The development of the magnesium industry in India for production of magnesium metal will not be an end in itself but will rather be the first step in the future development of fabrication and allied industries which will be the spontaneous outcome of the extraction of this light metal.

Acknowledgments

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