

NOTES ON THE MAGNESIUM INDUSTRY1. INTRODUCTION

The following notes have been prepared to supplement the information already compiled by those interested in the establishment of the magnesium industry in Tasmania using the Smithton dolomite as the raw material.

The possibilities of producing metallic magnesium and magnesium salts are being considered and so information and statistics on both have been prepared. As the dolomite would have to be treated for the separation of the calcium content and preparation of a magnesium compound suitable for production of metallic magnesium, it would appear that the production of one or more magnesium salts for marketing could readily be achieved. Moreover, as there appears to be possibilities of marketing other magnesium salts within the British Empire, the preparation of these is well worth considering especially oxide, carbonate, chloride and sulphate.

11. METALLIC MAGNESIUMA. Historical Notes & Statistics.

The following notes present a brief account of the metallic magnesium industry during recent years. The facts and figures have been derived from numerous sources in the Geological Survey library.

It is extremely difficult to obtain statistics for production, consumption, export, import etc.

This is due firstly to the fact that the records of production in the magnesium industry as a whole are given for the raw material (mainly magnesite), and secondly to the fact that there is a disinclination on the part of some producers to disclose figures.

Germany.

Germany appears to have been the first country to produce metallic magnesium on a commercial scale. The process consisted of electrolysis of fused carnallite in a closed cell with recovery of the chlorine.

Germany has always been, and still is, the largest producer in the world. The largest producer both in Germany and in the world is the I.G. Farbenindustrie with its plant at Eberfelds (Ruhr). The metal is marketed as Elektron - a magnesium-zinc alloy. The process involves electrolysis of magnesium chloride.

Other plants are situated at Hemelingen near Bremen (the Aluminium-und-Magnesium fabrick A.G.) and at Bitterfeld.

It is stated that the production in 1925 was 1500 tons and that no figures have been published since.

For 1928, the current production was stated to be 4500-5000 tons, but a more conservative estimate was 2500-3000 tons.

For 1929, it was unofficially stated that the production might be as high as 10,000 tons but a more conservative report gave the figure at 2000 tons.

United States of America.

Prior to 1915, the U.S.A. imported its requirements of magnesium from Germany, but in that year it began to produce the metal. The number of producers ranged from 3 to 5 up till 1919, but from 1920-1927 there were only two producers and at present there is only one.

These two producers were the American Magnesium Corporation of America with its plant at Niagara Falls, N.Y. and the Dow Chemical Company at Midland. The American Magnesium Corporation used a process similar to that for the production of aluminium, the raw material being however selected caustic calcined magnesia made from California magnesite. This corporation ceased production in 1927 and now purchases its requirements from the Dow Chemical Company. It also affiliated with the U.S. Aluminium Company and moved its fabricating plant to Cleveland, Ohio.

The Dow Chemical Company produces metallic magnesium from magnesium chloride recovered as a by-product from its salt wells at Midland.

The Electron Metals Corporation of America formerly imported the metal from Germany but suspended operations in 1924.

It was reported that a new company - the U.S. Metallic Magnesium Company was formed in 1929, but no further information is available and no production has been reported.

The industry in America was helped by the introduction of a new tariff in 1922 providing for a duty of 40 cents per pound on metallic magnesium and 40 cents per pound of metallic content plus 20% of the foreign market value of manufactured forms. The same duties have continued in force until 1930 and probably to the present day.

Recent figures for new ingot magnesium produced and sold in the United States are:

1928	521,075 lbs
1929	1,329,669 "
1930	1,173,557 "

The following table shows the figures for domestic magnesium sold or used by producers from 1917-1927 and includes all forms:

	<u>Pounds</u>	<u>Value</u>	<u>Average Price.</u>		<u>Sheet Wire & Castings.</u>
			<u>Ingot</u>	<u>Powder</u>	
1917	115,813	\$ 233,626	2.02		
1918	284,118	615,217	1.81	2.67	
1919	127,465	247,302	1.83	2.85	
1920	123,800	233,200	1.60	2.75	
1921	48,000	86,000	1.30	2.36	
1922	60,000/	89,000/	1.60	1.13	
1923	125,000/	155,000/	1.25	1.00	3.60
1924	128,000/	150,000/	1.07	1.10	3.50
1925	245,000	274,000	0.86	1.63	3.00
1926	322,650	390,400	0.80	1.64	2.90
1927	366,400	441,700	0.90x	1.56	

/ Estimated

x Average quotation in E. & M.J.

The figures for the succeeding years are given below but refer only to new ingot magnesium sold or used by the producer.

	<u>Pounds</u>	<u>Value</u>	<u>Average value per lb.</u>	
1928	530,782	\$ 289,658	A	0.546
1929	908,351	512,313		0.562
1930	559,631	268,864		0.481
1931	580,463	199,633		0.344

The above tables show the great increase in the use of the metal and also the large and continuous decrease in price especially of the ingot metal.

The following figures represent the imports of magnesium for consumption and show how the imports have declined to a negligible amount, mostly in the form of powder.

	<u>Pounds</u>	<u>Value</u>
1918 (July-December)	11,899	\$ 16,259
1919	13,239	13,583
1920	29,275	25,055
1921	39,913	30,592
1922	182,939	54,448
1923	13,974	11,576
1924	8,738	6,561
1925	8,326	7,070
1926	10,117	4,750
1927	7,131	8,402
1928	12,039	11,890
1929	3,490	6,539
1930	5,689	19,599
1931	2,454	2,580

France.

France produces some magnesium but also imports the metal as ingots mainly from Germany.

A pure metallic magnesium (known as michel or maximum metal) is made at Messieres, Savoy. The Societe Electro-Chemie makes shapes, castings and forgings at Mantupet.

In 1930, a new company was being organised to produce metal and alloys from molten chloride made by treating magnesite with hydrochloric acid which is obtained by the action of hydrogen upon the chlorine released at the anodes of the magnesium cells. The arrangement is being sponsored by Cie Alais Froges et Camargine and the Societe d'Electro-Chemie et d'Electro-Metallurgie d'Ugine, and the plant was to be at Martigny.

Available figures for the production of metallic magnesium are given in kilograms:

1924	-	22,160	:	1927	-	35,000
1925	-	35,300	:	1928	-	52,000
1926	-	36,000	:	1929	-	56,000

The available figures for imports and exports are as follows (in long tons) :-

<u>Year</u>	<u>Imports</u>	<u>Exports</u>
1920	2	2
1921	1	1
1922	4	-
1923	2	12
1924	1	5
1925	8	-
1926	-	1
1927	55	-
1928	38	1
1929	52	2
1930	44	23
1931	71	7

United Kingdom.

The only recorded English producer is the Magnesium Company with its plant at Wolverhampton. The plant was apparently established during the Great War and worked as late as 1921 and is possibly even now producing judging by the export figures for domestic produce given below.

Very little information and no production figures are available. The electrolysis of fused chloride is the process used, further details of which are given later.

The only statistics available are those of exports and imports which are as follows (in long tons):-

<u>Year</u>	<u>Exports</u> <u>(Domestic produce)</u>	<u>Imports</u> <u>(Less re-exports)</u>	<u>Re-Exports</u>
1920	17	18	
1921	9	11	
1922	1	8	
1923	3	25	
1924	9	21	
1925	10	21	
1926	19	52	
1927	9	26	
1928	9	68	
1929	12	149	
1930	14	46	
1931	46	62	

Italy.

Italy imports magnesium ingots mainly from Germany. In 1929 it was reported that one or more plants were to be erected at Venice for producing aluminium, magnesium and alloys, but as far as is known they were not erected.

Switzerland. It was reported in 1929 that a new factory was to be erected to produce 300 tons of magnesium in 1930, but no further information is available.

Russia.

It was reported in 1930 that production on a large scale was contemplated. The Ukrainian salt lake deposits are situated near the Dneiper River hydro-electric plant and the Soviet Chemical Trust announced its intention of producing 300 tons of magnesium per annum.

Another plan was stated to have called for the construction of plant to produce 1000 tons of magnesium annually.

Canada.

A plant was established in 1917 by the Shawinigan Electro-Metals Co. Ltd. at Shawinigan to produce the metal by electrolysis of fused chloride. The production was intermittent and it is not known if it is still in operation. No production figures are available.

Norway.

In 1921, the Aktieselskabet de Norske Saltverker started the erection of a factory at Fjotlandsvaag, Norway, but no further information is available.

B. Raw Materials.

Several kinds of raw materials have been used as the starting point for the production of metallic magnesium.

- (1) Salt Deposits. Salt deposits such as those of Stassfurt contain magnesium chloride chiefly in the form of carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$), which has been used in Germany for the production of magnesium.
- (2) Salt Lake deposits, brines etc. These contain magnesium salts, chiefly chloride and sulphate. The Dow Chemical Co. in U.S.A. recover the magnesium chloride as a by-product from its salt industry and use it for making magnesium. In Russia, it was proposed to use salt lake deposits to give a product for making magnesium.
- (3) Magnesite ($MgCO_3$). Magnesite has been used as

the raw material, but calcination to yield the oxide, or treatment with acid to yield a salt such as the chloride has been necessary. The former method was used by the American Magnesium Corporation in U.S.A., and the latter was contemplated in France in 1930.

- (4) Dolomite. Dolomite would have to be treated similarly to magnesite so as to yield the oxide, chloride, or other salt. In addition, the calcium content has to be separated.

C. Processes.

A large number of processes have been investigated of which the following are the most important.

- (1) Direct reduction of the oxide by carbon. This resulted in a low grade product in a powdery form. It was formerly used commercially, but is not now employed.
- (2) Electrolysis of the fused oxide in a bath of magnesium fluoride. This process was used by the American Magnesium Corporation. A special electric furnace was used with a lining of unfused electrolyte produced by cooling from the water-jacketed parts of the furnace. Magnesium oxide is added, carbon monoxide being given off at one electrode and magnesium formed at the other.
- (3) Electrolysis of the fused chloride in a bath of sodium and potassium chlorides, magnesium chloride being added continuously. The electrolysis of fused chloride is used by the Dow Chemical Company in U.S.A.; was formerly used in Canada; was used by the Magnesium & Co. in England; and was contemplated by the new company forming in France in 1930. It is also probably used by the I.G. Farbenindustrie in Germany. The recent trend has been in the way of dispensing with the sodium and potassium chlorides that were added, and making the process a continuous one. These developments have been facilitated by the production of dehydrated magnesium chloride on a commercial scale, and still further when it became possible to use a partly dehydrated magnesium chloride.
- (4) Electrolysis of Carnallite. This resembles that of the pure chloride except that it would not be necessary to add potassium chloride but rather to withdraw it from time to time. It was formerly used in Germany.
- (5) Reduction of fused dehydrated magnesium chloride by metallic sodium. The consumption of sodium (2 lb. for each 1 lb. of magnesium produced) and the preparation of dehydrated chloride forbid its consideration.
- (6) Reduction of fused magnesium chloride by metallic aluminium.

Of the above the electrolysis of fused chloride appears to be the most common process. This is particularly applicable when magnesium chloride (or the double chloride) is obtainable from salt deposits, brines etc. In other cases the chloride would have to be prepared by hydrochloric acid treatment of the raw material, e.g. dolomite, used.

The chloride process involves:

- (a) Preparation of anhydrous magnesium chloride as such or in admixture with alkali chlorides.
- (b) Electrolysis of the magnesium chloride in a cell at low voltage.
- (c) Purification of the resulting metal.

Further details of the above are given below.

- (a) In preparing anhydrous from hydrated chloride the object is to prevent the chloride being converted to oxide on heating.

Numerous patents have been taken out in connection with this preparation. The Dow Chemical Company process involves heating of the hydrous chloride at low temperatures with admixture of 25% sodium chloride and a little ammonium chloride, whereby 50% of the water is driven off. The partly dried mix is then cooled and reheated at higher temperatures until the remaining water is removed.

The Magnesium Company process involves heating for several hours at 150° in dry air, part of the water being driven off and yielding a product with MgCl₂ - 70%, MgO - 4% and H₂O - 23%. This is reheated in a current of hydrochloric acid gas at 300°C when the remaining water is removed, and the oxide converted to chloride, the product containing over 99% MgCl₂.

Many other patents exist, but the processes need not be discussed at this stage.

The process shown in the attached outline prepared by Mr. Reynolds is similar to that of the Magnesium Company.

- (b). The anhydrous chloride or a suitable mixture with alkali chlorides, is electrolysed at 675° to 725°C at a voltage of 5 to 8 volts. Magnesium chloride is added from time to time in order to make the process continuous and not a batch process.

Several types of cells are used. In a single stage process the cell is a cylindrical or rectangular iron box having carbon anodes, the iron cell acting as the cathode. In some cells a steel cathode may be suspended in the bath. Preliminary heating is necessary, but when electrolysis begins no external heating is necessary. The molten magnesium collects at the cathode

and eventually rises to the surface of the bath and is ladled out from time to time. Chlorine is liberated at the anode and is swept out of the cell and recovered.

The Magnesium Co. in England used a two-stage process. The cell is of cast steel with a fire-brick lining fitted with a gas-tight cover carrying graphite anodes. The cell is charged with liquid lead for the cathode and this is covered with electrolyte into which the anodes dip. The bath and molted lead are both circulated. The first operation produces a lead-magnesium alloy at the cathode, and in the second stage this alloy acts on the anode in another cell. The cells are in series, the first having a voltage of 5 and the second a voltage of 2.

(c) The magnesium from the chloride process has to be purified to remove traces of chlorides etc. and several processes have been used for this purpose. Distillation appears to be the most general and yields a very pure product.

Another involves the use of "elrasal" which is a mixture of alkaline earth chlorides, flourides and magnesia.

D. Treatment of the Dolomite.

A method which readily suggests itself for the separation of the calcium and magnesium in the dolomite is that used in the preparation of basic magnesium carbonate, magnesia, magnesia alba etc. from dolomite. This process is illustrated in the attached flow sheet prepared by the Magnesia Association of America. It could be carried as far as the precipitation of the calcium carbonate and the solution of the magnesium as bicarbonate. Hydrochloric acid treatment would then yield the chloride if electrolysis of fused chloride was the method to be adopted for the preparation of metallic magnesium.

At the same time, the bicarbonate solution could be used for the production of sulphate, chloride, oxide, magnesia alba etc. as outlined in the attached chart prepared by Mr. J. Reynolds.

III. MAGNESIUM SALTS.

Little need to said upon the subject of magnesium salts except to indicate the possibilities of marketing within the British Empire. Every member of the Empire is an importer of magnesium salts as will be seen from the statistics of imports given below. The figures given are for imports less re-exports and there are no exports of domestic produce except for Great Britain and small amounts of magnesium sulphate intermittently from South Africa and Canada. All the figures given below are taken from the Statistical Summaries of the Imperial Institute on the Mineral Industry of the British Empire and Foreign Countries.

Great Britain.

The imports are of magnesium slats including chloride and sulphate.

	<u>In long tons.</u> Exports of Domestic Produce	Imports less re-exports.
1920	6097	10745
1921	2709	12919
1922	3271	20400
1923	4217	20502
1924	4356	21357
1925	4754	25661
1926	3766	25667
1927	3393	28549
1928	3437	33390
1929	3647	40016
1930	3655	25964
1931	3782	26159

Australia.

Imports (In long tons).

		<u>Magnesium Carbonate</u>	<u>Magnesium Chloride.</u>	<u>Magnesium Sulphate.</u>
1920	8	67	43	141
1921	12	86	110	176
1922	4	57	49	267
1923	11	65	205	320
1924	56	114	170	367
1925	415	209	286	430
1926	190	74	375	549
1927	190	196	310	790
1928	184	232	229	1413
1929	244	182	387	1452
1930	137	153	332	1369
1931	43	94	37	626

India.

Imports (In long tons)

	<u>Magnesium Chloride</u>	<u>Magnesium Sulphate</u>	<u>Others</u>
1920	2929	410	11
1921	2331	440	9
1922	3477	2193	4
1923	3825	1862	27
1924	4131	1553	165
1925	3590	1883	82
1926	3001	2073	53
1927	2151	2994	117
1928	1343	2161	54
1929	1895	2230	475
1930	1779	2987	32
1931	1827	1289	17

Canada
Imports (In long tons).

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	<u>Magnesium Oxide</u>	<u>Magnesium Sulphate.</u>
1920	222	-
1921	221	722
1922	191	1412
1923	356	1642
1924	170	1999
1925	133	1908
1926	119	1903
1927	131	2446
1928	332	2240
1929	949	2290
1930	1212	2291
1931	4741	1839

South Africa.
Imports (In long tons).

	<u>Magnesium Sulphate</u>	<u>Magnesium Carbonate</u>	<u>Magnesium Chloride.</u>
1920	111	-	-
1921	42	-	-
1922	111	-	-
1923	196	-	-
1924	-	184	-
1925	-	214	546
1926	-	262	237
1927	-	284	394
1928	-	440	429
1929	-	438	441
1930	-	395	363
1931	-	492	227

New Zealand
Imports (In long tons).

	<u>Magnesium Sulphate.</u>
1928	201
1929	187
1930	242
1931	235

SUMMARY.

It will be realised from the above that there is a possibility of developing markets for magnesium compounds in Great Britain, Canada, South Africa, India and New Zealand.

The production of such would represent an industry of appreciable size. At the same time it would permit of the production of magnesium bicarbonate or chloride at a comparatively low cost (due to the spread of the overhead charges over the magnesium compound industry) so that a low-priced material would be available for the production of metallic magnesium.

The bicarbonate could be prepared from the Smithton dolomite by an established method. The Smithton dolomite deposits are very extensive and part is of very good grade. The dolomite could be quarried by sub-surface methods and the overburden of sand etc. is not deep.

Mines Department, HOBART
28th March, 1933

(signed) P.B. Nye.
GOVERNMENT GEOLOGIST.