Magnesium from Olivine

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THE presence in the Tennessee Valley of extensive deposits of olivine, a silicate of magnesium and iron that contains approximately 28 per cent magnesium, has been recognized since 1896 when Lewis[8] published a survey of basic magnesium rocks of western North Carolina. A recent field survey by T.V.A.[7] showed that more than two hundred million tons of high-grade olivine occurs above local drainage levels in western North Carolina and northern Georgia.

Except for sporadic attempts to work the olivine for its nickel and chromium contents,[10] the ore received little attention industrially until 1926 when Goldschmidt[3] suggested its use in the manufacture of refractories. Only one instance is recorded of an attempt to utilize the ore commercially for its magnesium content;[11] in this case a process was used in which olivine was treated with sulphuric acid, the resultant mixture was leached with water, and the leach solution was purified and evaporated to form epsom salts, which was the end product.

As a part of its program of contributing to the development of the natural resources of the region, the Tennessee Valley Authority became interested in the olivine deposits as a source of metallic magnesium because of their high magnesium content and proximity to hydroelectric power. Studies were undertaken to determine the feasibility of producing magnesium chloride by

extraction of olivine. The experimental work was carried out successively at the T.V.A. Minerals Testing Laboratory, Norris, Tenn., at the Georgia State Engineering Station,* Atlanta, Ga., and at the T.V.A. laboratory at Wilson Dam, Ala. The present paper describes a process, developed through the pilot-plant stage, whereby magnesium chloride suitable for reduction to metallic magnesium can be prepared from olivine by extraction with hydrochloric acid and subsequent purification.

Research on the magnesium-from-olivine process, originally intended for peacetime use, was given impetus by the shortage of magnesium that existed at the beginning of the current world war. By the time the process was sufficiently developed to justify a proposal for its inclusion in the war program, the shortage had been met by expansion and development of other processes. However, it is believed that the magnesium-from-olivine process may have advantages that will warrant consideration of its use after the war, when the economics of the various processes rather than production on a wartime scale will be the criterion for commercial production of magnesium.
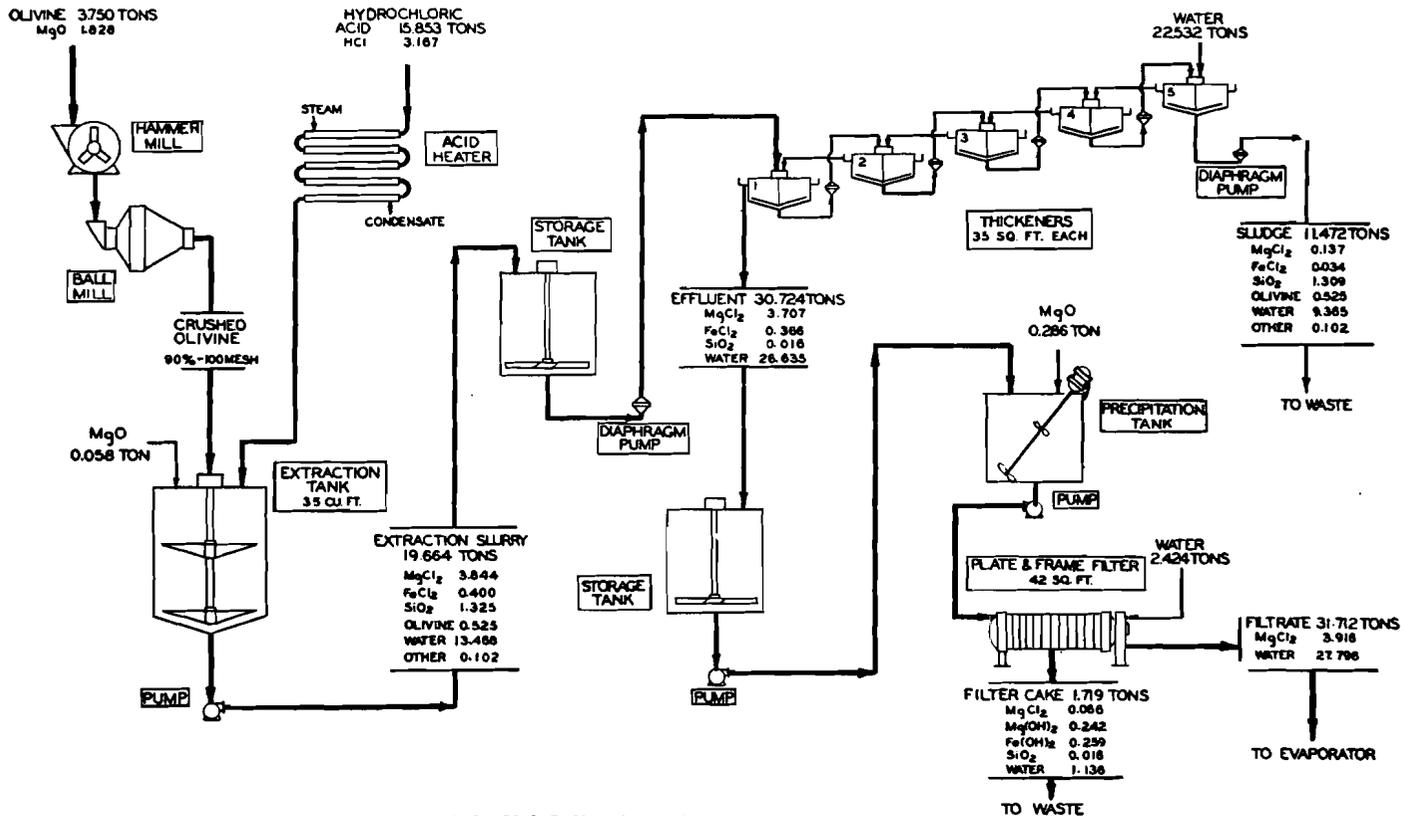
DESCRIPTION OF PROCESS

Metallic magnesium is produced electrolytically by the Dow and the Elektron

OLIVINE 3.750 TONS
MgO 1.828

HYDROCHLORIC
ACID 15.853 TONS
HCl 3.167

WATER
22.532 TONS

HAMMER MILL

STEAM

ACID HEATER

BALL MILL

CONDENSATE

DIAPHRAGM PUMP

CRUSHED OLIVINE
90%-100MESH

STORAGE TANK

THICKENERS
35 SQ. FT. EACH

SLUDGE 11.472 TONS
MgCl₂ 0.137
FeCl₂ 0.034
SiO₂ 1.309
OLIVINE 0.525
WATER 9.365
OTHER 0.102

$MgCl_2$ ... (see table)

EFFLUENT 30.724 TONS
MgCl₂ 3.707
FeCl₂ 0.386
SiO₂ 0.016
WATER 26.635

MgO
0.058 TON

EXTRACTION TANK
35 CU. FT.

MgO
0.286 TON

TO WASTE

DIAPHRAGM PUMP

PRECIPITATION TANK

PUMP

EXTRACTION SLURRY
19.664 TONS
MgCl₂ 3.844
FeCl₂ 0.400
SiO₂ 1.325
OLIVINE 0.525
WATER 13.468
OTHER 0.102

STORAGE TANK

PLATE & FRAME FILTER
42 SQ. FT.

WATER 2.424 TONS

FILTRATE 31.712 TONS
MgCl₂ 3.916
WATER 27.796

PUMP

PUMP

FILTER CAKE 1.719 TONS
MgCl₂ 0.086
Mg(OH)₂ 0.242
Fe(OH)₂ 0.259
SiO₂ 0.016
WATER 1.136

TO EVAPORATOR

TO WASTE

NOTE: ALL VALUES GIVEN ARE BASED ON THE PRODUCTION OF ONE TON OF Mg PER 24 HOURS

FIG. 1.—FLOWSHEET FOR PRODUCTION OF MAGNESIUM CHLORIDE BY EXTRACTION OF OLIVINE WITH HYDROCHLORIC ACID.

processes. The process developed by T.V.A. produces a partially hydrated magnesium chloride suitable for reduction by the Dow process. Since the Elektron process requires an anhydrous cell feed, the magnesium chloride produced by the T.V.A. process cannot be used in the Elektron-type cell. At present, magnesium chloride for reduction by the Dow process is prepared by methods[13] that include evaporation and fractional crystallization of brines; chloridization of dolomite and of sea-water magnesia by treatment with hydrochloric acid; and treatment of dolomite with a soluble chloride, usually by-product calcium chloride. When hydrochloric acid is used to prepare magnesium chloride, the acid is made from the chlorine obtained from the reduction of magnesium chloride. The various processes have been described in the literature, and it is not within the scope of this paper to review them at length. It is apparent, however, that the present methods for preparing magnesium chloride cell feed of suitable purity and without excessive loss of hydrochloric acid are not simple.

The process developed by T.V.A. for the production of magnesium from olivine consists of the following principal steps.

1. Finely ground olivine is extracted with aqueous hydrochloric acid to produce an impure magnesium chloride solution and a residue consisting principally of silica.

2. The siliceous residue is separated from the solution by continuous countercurrent decantation in thickeners.

3. Magnesia is added to the clarified impure solution to precipitate the iron and minor impurities as hydroxides, and the precipitate is separated from the solution by filtration.

4. Magnesium chloride cell feed is prepared from the purified solution by evaporation and dehydration.

5. The dried magnesium chloride is charged to an electrolytic cell to produce metallic magnesium and chlorine gas.

6. The chlorine gas is converted to hydrochloric acid by reaction with steam and coke, and the acid is recycled to step 1.

Although the pilot plant used in the study of this process included equipment for carrying out all these steps, the experimental work was directed principally toward development of the first three steps, in which the process necessarily differs from other chloride electrolytic magnesium processes. Fig. 1 is a quantitative flowsheet, based on a 6-week period of operation of the part of the pilot plant that is operated for the production of purified magnesium chloride solution from olivine. The pilot plant had a capacity of 700 lb. of magnesium chloride (13 per cent solution) per 24 hr. Fig. 2 is a general view of the pilot plant showing the extraction, purification, and reduction units. Since preparation of magnesium from the purified solution and conversion of the resulting chlorine to hydrochloric acid (steps 4, 5, and 6) were carried out by methods commonly used in other processes for producing magnesium, only a brief description of the methods used in carrying out these steps in the pilot plant is presented in this paper.

The Olivine Used

Olivine, a mineral of igneous origin, consists of a solid solution of magnesium and ferrous orthosilicates and usually is designated by the formula $(MgFe)_2SiO_4$. It is light green, has a specific gravity of 3.2, and resembles some types of sandstone in that it has a granular, friable structure.

The olivine used in this work was obtained as a carload lot in the form of 4-in. to 6-in. lumps. It had been quarried from a deposit near Balsam, N. C., which had been shown by a field survey[7] to be typical of high-grade olivine available at several localities in western North Carolina. The Balsam deposit was estimated to contain 17 million tons of essentially unaltered olivine. The composition of this olivine, as determined chemically and spectrographically, was:

| Constituent	Per Cent
MgO	48.71
SiO$_2$	41.08
FeO	7.06
Fe$_2$O$_3$	1.28
Cr$_2$O$_3$	0.50
CaO	0.00
Al$_2$O$_3$	0.04
NiO	0.44
MnO	0.18
Cu	< 0.01
B	Not detected
Ignition loss	0.47
Total	99.77

Petrographic analysis[7] showed that the olivine was of crystal size ranging from about 0.1 to 5 mm. It contained a small amount of chromite and magnetite, occasional small crystals of chlorite, and thin seams of chrysotile.

The olivine was crushed in a jaw crusher to about 1-in. size and was then run through a hammer mill that reduced the ore to sand sizes in one pass. The product of the hammer mill was similar to quartz sand in grindability. It was ground in a ball mill and was dry-screened through a 100-mesh sieve. In preparing this olivine and in working with other samples of olivine, it was noted that the chromite was considerably harder than the olivine. This difference in hardness, which resulted in differential grinding and a concentration of chromite in the oversize, suggests the possibility of obtaining a salable chromite concentrate as a by-product.

EXTRACTION

Laboratory Results

The reaction between olivine and hydrochloric acid may be represented by the equation:

$$(MgFe)_2SiO_4 + 4HCl\ (aq.) = 2(MgFe)Cl_2 + SiO_2.XH_2O$$
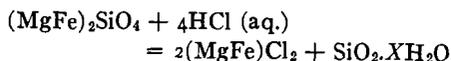
Maximum conversion of hydrochloric acid to magnesium chloride was considered more important than maximum extraction of magnesium from olivine, because any acid not converted to magnesium chloride during extraction would have to be neutralized with magnesia, which is relatively expensive. Consequently, the principal objectives for the extraction were: (1) to convert as much as possible of the hydrochloric acid to magnesium chloride, (2) to produce the siliceous residue in a nongelatinous form, in which it could be readily separated from the solution, and (3) to extract as high a percentage of magnesia from the olivine as was consistent with the first two objectives.

Preliminary work[6] showed that the second objective—that is, the separation of silica—could be attained by a method that consisted of absorbing hydrogen chloride gas on the moistened surface of olivine particles. The magnesium chloride so formed was recovered by leaching, which left a residue of silica and unextracted olivine. Further studies of this method showed that inherent mechanical difficulties prevented efficient utilization of acid and olivine. The method was abandoned because of these difficulties, and the present process for extracting fine-ground olivine with aqueous hydrochloric acid was developed.

Preliminary extraction tests made with varying proportions of olivine and hydrochloric acid showed that it was feasible to extract about 86 per cent of the magnesium from olivine and simultaneously to obtain about 97 per cent reaction of the acid to form chlorides of magnesium and iron. The preliminary tests showed that, regardless of the ratio of acid to olivine used in the extraction, the mol ratio of magnesium to iron in the extract was about 12, which was approximately equal to the mol ratio of magnesia to ferrous oxide in the olivine; this indicated that the extraction was not selective.

The settling rate and bulk density of the siliceous residue were increased by increasing the concentration of the acid used and

the temperature of extraction; both factors had a dehydrating effect on the silica formed. An acid concentration of 20 per cent HCl was found to be sufficiently high with vacuum applied for 30 min. The degree of hydration of the silica residue in these tests, as determined by drying at 120°C., decreased from about 35 to about
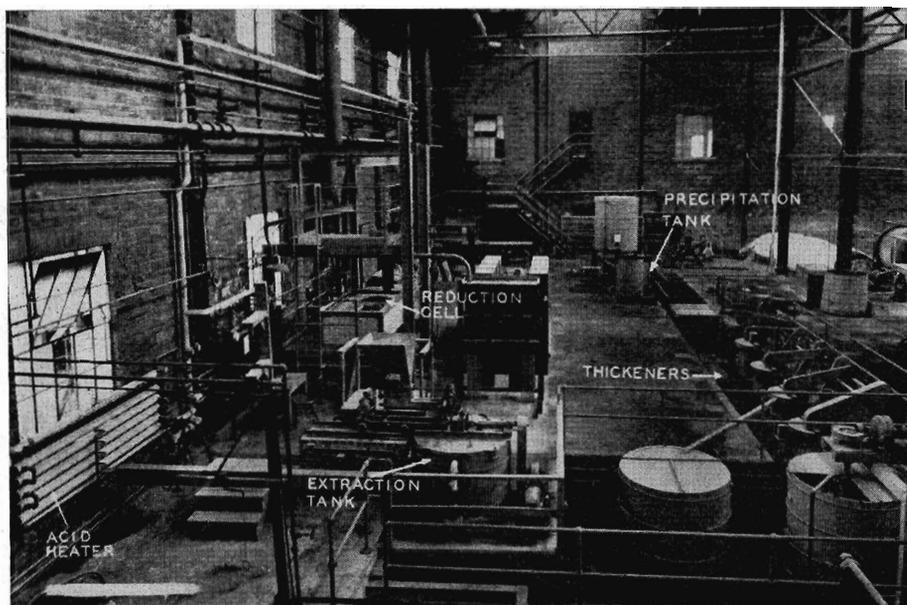

FIG. 2.—PILOT PLANT FOR EXTRACTION OF MAGNESIUM FROM OLIVINE.

to permit production of the silica in a favorable condition for separation by settling. Higher concentrations, though beneficial to the settling properties of silica, caused difficulty due to loss of acid as fume. It is feasible to produce acid of 20 per cent concentration from magnesium chloride reduction-cell gases,[9] but it was questionable whether these gases were suitable for the economic production of acid of higher concentration.

In a series of tests in which the acid concentration was 20 per cent HCl and the extraction temperature was varied, it was observed that the residue produced had good settling properties when the temperature was in the range 90° to 110°C. Samples of the residue were separated from the solution by filtering on a Buchner funnel; the residue was washed with water and then was allowed to remain on the filter

20 mols of H_2O per mol of SiO_2 when the temperature of extraction was increased from 60° to 105°C. The residues produced at the lower temperatures were of large bulk, because of their high degree of hydration. and did not settle well.

Tests of the effect of temperature on percentage of magnesium extracted from olivine showed that when the temperature was increased from 70° to 110°C. the amount of magnesium extracted increased from 30 per cent to 80 per cent at an extraction time of 30 min. (Fig. 3). Although it was possible to extract a satisfactorily high percentage of magnesium from olivine at temperatures in the range 80° to 100°C. with prolonged extraction, extended extraction periods at temperatures much below 100°C. were undesirable because these conditions tended to produce a gelatinous type of silica. When extraction was

carried out at or near boiling temperature, the reaction was practically complete in 30 min. or less, and the residue had good settling properties.

that could be pumped readily; unagitated mixtures yielded a stiff, gelatinous mass. It was desirable to add the acid and olivine to the reaction vessel simultaneously while

ACID/OLIVINE RATIO, 89 % STOICHIOMETRIC
ACID CONCENTRATION, 20 % HCL
OLIVINE PARTICLE SIZE, - 100 MESH
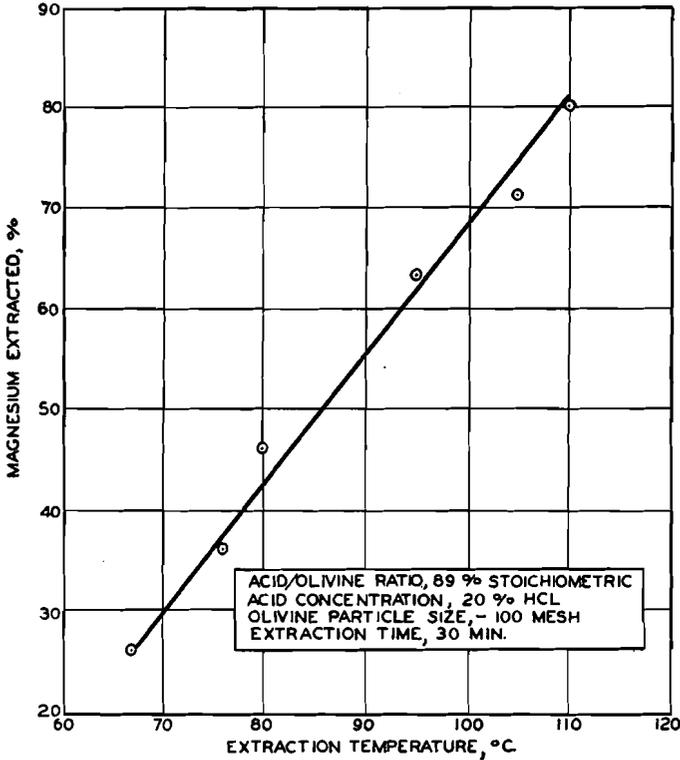EXTRACTION TIME, 30 MIN.

Fig. 3.—Effect of extraction temperature on percentage of magnesium extracted from olivine with hydrochloric acid.

Since the reaction between olivine and hydrochloric acid is exothermic, it was convenient to utilize the heat of reaction to raise the temperature of the mixture to boiling. To start the reaction at a sufficient rate to induce boiling, it was usually necessary to preheat either the olivine or acid. Preheating the acid to about 60°C. was generally sufficient to cause boiling of the reaction mixture in uninsulated vessels. It was not practical to use heating coils in the reaction vessel because a silica scale deposited on the heated surfaces.

Thorough agitation during the reaction was essential for production of a fluid slurry

maintaining good agitation; this procedure released the heat of reaction gradually and prevented too vigorous boiling or foaming. The particle size of the olivine was relatively unimportant in all sizes finer than 100 mesh. Larger sizes were difficult to keep in suspension during extraction.

Pilot-plant Operation

Data from the small-scale tests were used in designing a pilot-plant extraction unit. Particular attention was given to use of materials of construction that would be adaptable to commercial-scale operation. The extraction vessel was a cylindrical steel

tank lined with Pyroflex and acidproof brick; the tank was 65 in. high and had an inside diameter of 45 in. Four bricks projected 4½ in. from the walls into the tank to serve as baffles. A 1-in. opening was provided in the center of the bottom for pumping out the reaction slurry. The agitator in the tank was made of yellow pine, and consisted of a vertical shaft, 2 by 2 by 64 in., on which were mounted two horizontal paddles, which described a 43-in. diameter circle. The wood had been treated with Bakelite Resinoid BR-5995 according to the manufacturer's instruc-

The extraction charge used in the pilot plant consisted of 210 to 238 lb. of minus 100-mesh olivine and 890 to 960 lb. of 20 per cent HCl. The feed rates for the acid and olivine were adjusted so that the charge was delivered to the reaction vessel in 30 min. The feed temperature of the acid was about 70°C.; the olivine was not preheated. After about half the charge had been added, the temperature of the mixture reached boiling (110°C.). After the charge had been added, the mixture was agitated for 10 min., and magnesia (chemical grade, 93 per cent MgO) was added

TABLE 1.—*Effect of Proportion of Acid to Olivine on Extraction of Magnesium and Acid Utilization*

Number of Tests Averaged	Composition of Charge			Magnesia Required[b] (93 Per Cent MgO), Lb.	Extraction of Magnesium, Per Cent	Utilization of Acid, Per Cent		
	Acid (20 Per Cent HCl), Lb.	Olivine, Lb.	Acid Used, Per Cent of Stoichiometric[a]			MgCl₂ from Olivine	MgCl₂ from Magnesia	FeCl₂ from Olivine
7	890	238	78.5	2.7	76.4	90.11	2.55	7.34
2	960	238	84.7	3.3	82.2	89.81	2.88	7.31
10	890	210	89.0	3.7	85.8	89.24	3.49	7.27
5	935	210	93.5	7.5	87.1	86.24	6.74	7.02

[a] Based on MgO and FeO content of olivine.
[b] For neutralization of free acid.

tions, to increase its resistance to attack by acid. The top of the shaft was held in a steel chuck connected to a motor and a speed reducer. The speed of rotation was 40 r.p.m. The reaction tank was provided with a steel cover, which was lined with Pyroflex and was fastened to the tank by means of swing bolts to facilitate replacement of the agitator. The temperature of the extraction mixture was measured by an indicating thermometer that had a 6-ft. bulb extension enclosed in a 1-in. Karbate well cemented to the brick lining. A 2-in. porcelain pipe entered the tank just below the cover and was connected with an exhaust fan for fume disposal. Olivine was charged to the tank by means of a hopper and screw feeder, and acid by gravity flow from a make-up tank through a glass plug cock and Pyrex double-pipe heat exchanger.

in amounts sufficient to combine with the free acid. Control of this operation was based on a color change of the mixture from green to gray, which occurred at a pH of about 4. Since the mixture was buffered in the range pH 4 to 5, control of this step was not difficult, although efforts were made to avoid overdosage of magnesia.

The pilot-plant extraction unit was operated for a total of 75 extractions. Operation was carried out by nontechnical personnel, and no difficulties were encountered. The wooden agitators were replaced after 30 extractions, at which time they were in a weakened condition, although none of them failed in service. The volumetric capacity required for extraction, based on the size of the pilot-plant unit, was 35 cu. ft. per ton of magnesium per 24 hr. From the standpoint of the chemistry

of the extraction procedure, there is no reason why it could not be made a continuous rather than a batch operation. Batch extraction was more convenient in the present work because of mechanical and corrosion problems, which would complicate the construction of a continuous extraction unit.

The principal variable investigated in the pilot-plant extraction was the proportion of acid to olivine. The data, averages of which are given in Table 1, show that increasing the ratio of acid to olivine from 78.5 to 89.0 per cent of stoichiometric* was desirable, since it resulted in a proportionate increase in the extraction of magnesia, from 76.4 to 85.8 per cent, without significantly affecting the amount of magnesia required for neutralization of free acid; the acid utilization by extraction of magnesia from olivine was substantially constant at about 90 per cent. A further increase in the ratio of acid to olivine to 93.5 per cent of stoichiometric was undesirable, since the magnesium extraction increased by only 1.3 per cent whereas the utilization of acid decreased by 3.0 per cent and necessitated a twofold increase in the quantity of magnesia required for neutralization of the free acid. In view of the relative costs of olivine and magnesia, it was considered desirable to use an acid-olivine ratio of about 89 per cent of stoichiometric rather than to use a higher ratio, which would require more magnesia than was justified by the improvement in extraction.

PURIFICATION

Laboratory Results

The impurities that are undesirable in magnesium chloride to be reduced to magnesium metal in electrolytic cells may be classified in two groups: (1) those that

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* Based on MgO and FeO content of olivine; Fe_2O_3 and other constituents were not considered in calculating the stoichiometric proportion of acid.

interfere with cell operation or introduce undesirable impurities into the magnesium, such as nickel, iron, chromium, copper, boron, and sulphate and (2) those that act as diluents to the cell bath and require periodic removal; this group includes magnesia, silica, and compounds of calcium and of alkali metals. It is desirable to obtain substantially complete removal of all members of the first group. Members of the second group can be considered to be admissible in small proportions, their allowable concentration being governed by an economic balance between their removal from the magnesium chloride and replacement of the electrolyte.

Chemical and spectrographic analyses of the olivine used during the present work showed that boron, calcium, copper, and aluminum were not present in sufficient quantities to require consideration and that iron, nickel, chromium, and silica would require removal. The manganese content of the olivine was considered beneficial to the electrolytic reduction step.[5]

The purification of the mixture resulting from extraction of olivine with hydrochloric acid involved separation of the insoluble residue from the impure solution, precipitation of dissolved impurities from the solution, and separation of the precipitate from the purified solution. Unextracted olivine, silica, and most of the chromium (present as chromite) were removed in the extraction residue. The dissolved impurities consisted principally of the chlorides of iron and nickel; traces of copper and chromium may have been present. Since all the dissolved impurities form insoluble hydroxides or basic salts at a pH well below 10.5, the pH at which magnesia is precipitated,[1] their separation in this way was the obvious procedure. It was desirable to precipitate the dissolved impurities by adding a basic compound of magnesium, such as magnesium oxide or hydroxide, in order to recover the chloride ion as mag-

nesium chloride and to avoid the introduction of other impurities. In commercial operation, magnesia for precipitation might be prepared from a part of the magnesium chloride produced, or sludge from the electrolytic cell might be used. Cell sludge consists of a mixture of magnesia, which is formed by unavoidable decomposition of a part of the magnesium chloride during dehydration, and entrained electrolyte.

In an early stage in the development of the purification step, consideration was given to two alternative procedures: (1) a one-step procedure in which magnesia was added to the extraction slurry in sufficient quantities to precipitate the dissolved impurities, after which the extraction residue and precipitated impurities were separated from the purified solution in one operation, and (2) a two-step procedure in which the extraction residue was separated from the impure solution, magnesia was added to the clarified solution to precipitate the impurities, and the precipitate was removed from the purified solution.

When magnesia was added to the hot or cold solution after separation of the extraction residue (procedure 2), adequate purification was obtained with a small excess of magnesia. Satisfactory purification of the solution was obtained by the one-step procedure when the slurry was cooled to room temperature before addition of the magnesia; however, the one-step procedure required a larger amount of magnesia than the two-step procedure to accomplish a comparable amount of purification. When the magnesia was added to the hot slurry that contained the extraction residue, adequate purification could not be obtained, even with a large excess of magnesia. Typical data obtained in these tests are given in Table 2.

The poorer results that were obtained when the solution was purified by addition of magnesia to the extraction slurry appeared to have been caused by a tendency of the pH to decrease with time until it reached a point at which the impurities were redissolved. This decrease in pH probably was caused by a reaction between the silica and magnesia. Since a pH of 7 or higher was necessary to ensure complete precipitation of iron and nickel, instability of the pH in this range rendered control of the operation unsatisfactory.

A further disadvantage of the one-step procedure was that magnesium oxychloride is formed[2] in appreciable amounts when

TABLE 2.—*Effect of Amount of Magnesia, Temperature of Solution, and Presence of Extraction Residue on Purification of Magnesium Chloride Solution*[a]

Magnesia Added, Per Cent of Stoichiometric[b]	Solution Temperature, Deg. C.	pH of Treated Solution	Composition of Treated Solution	
			$\frac{Fe}{MgCl_2} \times 100$	$\frac{Ni}{MgCl_2} \times 100$
Extraction Residue not Removed before Precipitation				
110	Room	6.7	0.22	0.013
120	Room	6.8	0.13	0.011
150	Room	7.3	0.01	<0.002
270	70	6.4	>0.10	
270	100	6.5	>0.10	
Extraction Residue Removed before Precipitation				
100	Room	7.5	0.021	
110	Room	7.3	0.012	
120	Room	7.8	0.001	<0.002
120	90	8.5	0.000	
120	108	8.0	0.001	

[a] Average composition of impure solutions: $\frac{Fe}{MgCl_2} \times 100 = 7.5$; $\frac{Ni}{MgCl_2} \times 100 = 0.17$.
[b] Stoichiometric magnesia requirement was calculated as that required to convert all chlorides, not already present as $MgCl_2$, to $MgCl_2$.

magnesia is added to neutral solutions having a magnesia concentration greater than 13 per cent by weight in accordance with the following equation:

$$MgCl_2 + Mg(OH)_2 = 2MgOHCl$$

To avoid loss of magnesia by formation of this compound, it would be necessary either to use acid less concentrated than 20 per cent HCl in the extraction or to dilute the extraction slurry before adding mag-

nesia. In the two-step procedure water added for washing the extraction residue served to dilute the solution to about 13 per cent $MgCl_2$. For these reasons the two-step purification procedure was considered preferable.

Several tests were made in which sludge from an experimental cell was used instead of magnesia for precipitation of iron and other dissolved impurities from solutions produced by extraction of olivine. The cell sludge contained about 25 per cent MgO; the remainder was principally the constituents of the electrolytic bath. Analysis of the cell sludge was as follows: MgO, 24.6 per cent; $MgCl_2$, 11.6; NaCl, 21.3; KCl, 21.4; $BaCl_2$, 10.6. The results of these tests showed that the cell sludge was as effective as magnesia in precipitating iron and nickel from solution, per unit of MgO.

Settling tests made with the extraction slurry indicated that it would be feasible to separate the impure solution from the extraction residue by sedimentation. The applicability of continuous countercurrent decantation would depend on whether gelling occurred, as has been noted in work with similar materials containing free acid.[12] Settling tests made in the laboratory corroborated the literature. When the slurry contained free acid, gelling occurred and the residue did not settle well; when the slurry did not contain free acid, gelling did not occur and settling was satisfactory. It was concluded that the use of thickeners for separation of the extraction residue would be feasible if the free acid in the extraction slurry was neutralized. Neutralization of the free acid was accomplished by adding a small amount of magnesia as described under Extraction. This procedure had the additional advantage that acidproof materials were not required for the thickener system. A corrosion test of mild steel in extraction slurry in which the free acid had been neutralized showed a satisfactorily low penetration rate of 0.002 in. per year.

Filtration of the extraction slurry was not a promising method for separating the extraction residue because atmospheric oxidation of the solute iron caused precipitation of ferric hydroxide in the pores of the filter cloth.

Either sedimentation or filtration was found to be suitable for separation of the precipitated impurities from the purified solution. Filtration appeared to be preferable because it was more adaptable to complete removal of the precipitated impurities.

Pilot-plant Operation

Pilot-plant equipment for separating the extraction residue from the impure solution by continuous countercurrent decantation consisted of five thickeners, each with a settling area of 3.14 sq. ft. and a depth of 3 ft. They were constructed of welded, $\frac{3}{16}$-in. mild steel. Although some contamination of the solution with iron from the thickeners was expected, this was not considered to be objectionable because the iron-removal step in the process followed the thickening step. The diaphragm pumps for the thickener sludge were steel-bodied and had ball check valves. All pumps and thickener rakes were driven from a central shaft. The piping was $\frac{3}{4}$-in. Saran, which was used because of the ease with which large-radius bends could be made with this material. Since extraction was carried out as a batch operation, a storage tank equipped with an agitator was installed between the extraction unit and the thickeners to provide a continuous feed for the latter. The No. 1 thickener overflow constituted the clarified impure solution; it was collected in a storage tank. The No. 5 thickener underflow was discharged to waste. Repulping was obtained by converging the influent streams of sludge and solution as they entered the feed wells. The system was operated on a 24-hr. basis for a period of 6 weeks, with an average daily capacity of 700 lb. of

$MgCl_2$ in the form of 13 per cent solution. The thickeners operated satisfactorily, and no formation of gel was noted. Based on the size of the pilot-plant thickener system the settling area requirement would be 35 sq. ft. per thickener per ton of magnesium per day.

Impure solution from the thickener system was treated in 180-gal. batches in a steel tank equipped with a mixer by adding magnesia until the pH of the solution reached or exceeded 7. The average magnesia requirement at this point corresponded to 17 per cent of the total magnesium chloride produced. The solution containing the precipitated impurities was pumped to a cast-iron filter press having seven 12 by 12 by 2-in. frames. Eight-ounce duck covered with a layer of

TABLE 3.—*Analysis and Flows of Thickener Feed, Overflow, and Underflow*

	Grams per Liter					Spe-cific Grav-ity	Flow Rates, Gal. per Hr.
	Mg^{++}	Cl^-	Fe^{++}	Fe^{+++}	Insol-ubles[a]		
Feed...	60.4	198.8	12.0	0.04	144.9	1.297	12.5
Over-flow.	37.4	113.6	6.2	0.01	1.6	1.127	22.5
Under-flow.	2.5	7.2	0.3	0.00	184.2	1.115	8.5
Water.							18.6

[a] Dried at 110°C.

30-lb. or 40-lb. Kraft paper or newsprint was found to be a satisfactory filter medium. The filter pressure was from 5 to 25 lb. per sq. in., with an average filtration rate of 0.43 gal. per sq. ft. per min. Although the filter press was a nonwashing type, a certain degree of washing was obtained by following each batch with 16 gal. of water. Based on the size of the pilot-plant filter, the filter requirement for the process would be 42 sq. ft. of filter area per ton of magnesium per 24 hours.

Data showing the flow rates and chemical composition of the feed, overflow, and underflow from the thickener system are given in Table 3. These data represent the

most effective operation of the system and indicate that during this period 98 per cent of the residue was removed by the thickeners as underflow and that the loss of chloride in the underflow was only 2.5 per cent of the chloride input. The data given in the flowsheet (Fig. 1), which are based on an average of the 6-week period of operation, indicate that about 3.8 per cent of the total chloride input was lost in the underflow.

The magnesia requirement for precipitation of metallic impurities from the clarified solution in the pilot plant was about 250 per cent of stoichiometric,

TABLE 4.—*Composition of Materials from the Precipitation Step*

Filter Cake		Purified Solution	
Constituent	Per Cent by Weight	Con-stituent	Per Cent by Weight, $MgCl_2$ Basis
$Mg(OH)_2$.....	8.4	Fe	0.012
$Fe(OH)_2$......	10.6	Ni	0.000
$Fe(OH)_3$.....	7.1	Mn	0.025
$Ni(OH)_2$......	0.78	Cr	0.000
SiO_2.........	9.0	SiO_2	0.004
$MgCl_2$........	3.5	SO_4	0.107
Moisture.....	52.1[a]	Ca	0.000

[a] Loss on drying at 110°C.

although small-scale tests (Table 2) had indicated that 120 per cent of stoichiometric was sufficient when no silica was present in the solution. The increased magnesia requirement in the pilot plant was attributed to the presence of silica in the clarified solution from the thickeners as shown by the analysis of the filter cake (Table 4). It is believed that the magnesia requirement can be decreased by better operation of the thickeners or by filtration of the thickener overflow for removal of silica.

The amounts of impurities in the purified solution were believed to be sufficiently low for production of a satisfactory magnesium chloride cell feed, with the possible exception of the sulphate content. Since the presence of sulphate was not suspected,

no provision was made for its removal, which presumably can be accomplished by addition of a small amount of barium chloride during the precipitation step. Barium chloride is not an objectionable impurity in magnesium chloride cell feed.[6]

A material balance over the extraction and purification steps of the pilot plant for the 6-week period of operation covered by this paper is represented by the data in the flowsheet (Fig. 1). The magnesium distribution in the system is shown in Table 5. These data indicate that 76.5

TABLE 5.—*Magnesium Distribution in Extraction and Purification Steps*
PER CENT

Input		Output	
Olivine..........	84.1	Unextracted olivine in sludge........	11.8
Magnesia (to extraction step)...	2.7	MgCl₂ in thickener underflow.......	2.7
Magnesia (to purification step)....	13.2	Mg(OH)₂ in filter cake............	7.7
Total..........	100.0	MgCl₂ in filter cake.	1.3
		MgCl₂ in purified solution........	76.5
		Total..........	100.0

per cent of the total magnesia added was recovered as magnesium chloride in the purified solution.

If it were assumed that the magnesia added to the extraction and purification steps was obtained by recycling material produced from magnesium chloride in a later step, such as cell sludge or magnesia obtained by hydrolysis of magnesium chloride, the net recovery of magnesia from olivine would be 72.1 per cent. The magnesia recycled would amount to 20.8 per cent of the total magnesium chloride produced. The recovery of chlorine in the purified magnesium chloride solution was 94.7 per cent of the chlorine input as hydrochloric acid. These results are an average of those obtained in operation of the pilot plant under various conditions, some of which were known to be unfavorable to high recovery. Various means by which it is expected that the recoveries

can be improved have been pointed out in the previous discussion.

STEPS COMMON TO OTHER ELECTROLYTIC MAGNESIUM PROCESSES

Other steps of the process were common to other processes for the production of electrolytic magnesium. These steps were included in the pilot plant in order to complete the cycle of the process and to supplement the information available in the literature. For this reason, and because complete data have not yet been obtained in some units of the pilot plant, these steps will be described only briefly.

Evaporating and Flaking.—Purified magnesium chloride solution was evaporated in an open-top, brick-lined, steel tank equipped with stainless-steel steam tubes. After the concentration of the solution reached 48 per cent $MgCl_2$, the hot solution was run from the evaporator to a water-cooled drum flaker, which produced magnesium chloride flake of approximately hexahydrate composition.

Drying.—The flake chloride was dried in a rotary drier, fired with by-product carbon monoxide gas, to a composition that corresponded to the dihydrate.

Electrolytic Reduction.—Electrolysis of magnesium chloride was carried out in a 4000-amp. cell of conventional design. The cell gases were sent to the acid-manufacturing unit for recovery as hydrochloric acid.

Acid Manufacture.—Hydrochloric acid was manufactured from chlorine, coke, and steam by the reaction:

$$2Cl_2 + 2H_2O + C = 4HCl + CO_2$$
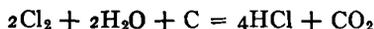
The equipment consisted of a shaft furnace, in which the reaction was carried out, a gas cooler, an absorber, and a storage tank. The capacity was about 1.2 tons of 20 per cent acid per 24 hr. Commercial chlorine was used in most of the pilot-plant operation described in this paper. During the latter part of the investigation,

when the electrolytic cell was being operated, cell gas was used as a source of acid.

CONCLUSIONS

The results of this investigation show that it is technically feasible to produce from olivine magnesium chloride believed to be of satisfactory purity for electrolytic production of magnesium, and that all steps of the process can be carried out with relatively simple equipment. The cost of producing magnesium chloride represents a relatively small part of the production cost of electrolytic magnesium; therefore economies in magnesium chloride production can have but small influence on over-all costs. However, the process would have important economic advantages because of the use of olivine as a raw material. These advantages may be listed as follows:

1. The geographic location of the olivine deposits is favorable because of the availability of large quantities of hydroelectric power. The location is also favorable with respect to markets, since a considerable portion of the aluminum industry, which uses large quantities of magnesium for production of alloys, is in the Tennessee Valley.

2. The magnitude and uniformity of any one of several olivine deposits in the Tennessee Valley region would ensure a supply of raw material for operation of a magnesium reduction plant for a period of time sufficient for amortization of the large capital investment required for electrolytic magnesium production.

3. The high magnesium content and high specific gravity of the olivine would favor low transportation costs per unit of magnesium and should allow considerable latitude in selecting a plant location to utilize existing electric power transmission and rail transportation facilities.

4. The possibility of by-product recovery is favorable. Although the olivine used in the experimental work was low in chromite, it would be feasible to use olivine containing several per cent of chromite.[7] Previous attempts to produce chromite from these deposits were not economically successful because the value of the chromite was insufficient to bear the costs of quarrying and crushing the olivine. If these costs were chargeable to magnesium production, there is little doubt that chromite recovery would be profitable. The feasibility of nickel recovery was not investigated; however, it is believed that a feasible process for extraction of the nickel from the filter cake could be developed.

Since the process described in this paper permits utilization of the economic advantages enumerated above, it is concluded that the production of magnesium from olivine warrants consideration in postwar industrial planning. Olivine was selected for this study in preference to serpentine because of the superior quantity and uniformity of the deposits of olivine in the Tennessee Valley. However, the two minerals are closely related in composition, chemical properties, and mineralogy, and tests have indicated that the process probably is applicable to serpentine as well as to olivine.

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