



CANADA

Dept. Mines & Technical Surveys
MINES BRANCH
SEP 20 1965
LIBRARY
OTTAWA, CANADA. 03

PRODUCTION OF HIGH-PURITY MAGNESIA

G. A. KENT

DEPARTMENT OF MINES AND
TECHNICAL SURVEYS, OTTAWA

MINERAL PROCESSING DIVISION

MINES BRANCH

RESEARCH REPORT

R 163

Price 50 cents

JUNE 1965

© Crown Copyrights reserved

Available by mail from the Queen's Printer, Ottawa,
and at the following Canadian Government bookshops:

OTTAWA

Daly Building, Corner Mackenzie and Rideau

TORONTO

Mackenzie Building, 36 Adelaide St. East

MONTREAL

Aeterna-Vie Building, 1182 St. Catherine St. West

or through your bookseller

A deposit copy of this publication is also available
for reference in public libraries across Canada

Price 50 cents' Catalogue No. M38 -1/163

Price subject to change without notice

ROGER DUHAMEL, F.R.S.C.
Queen's Printer and Controller of Stationery
Ottawa, Canada
1965

Mines Branch Research Report R 163

PRODUCTION OF HIGH-PURITY MAGNESIA

by

G. A. Kent

ABSTRACT

This investigation was carried out to produce magnesite, or magnesia, with low iron content. Flotation and magnetic separation of uncalcined magnesite ore yielded concentrates in the order of 2% Fe (as Fe_2O_3) and 0.5% SiO_2 . Calcination of the concentrates, followed by flotation and magnetic separation, further reduced the iron to about 1% Fe_2O_3 and the silica to about 0.4%. Leaching calcined ore or concentrate with dilute acetic acid produced magnesia containing less than 0.01% Fe_2O_3 and low silica. A procedure for producing high-grade magnesia is suggested.

* Senior Scientific Officer, Industrial Minerals Milling Section, Mineral Processing Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

Direction des mines

Rapport de recherches R 163

LA FABRICATION DE MAGNÉSIE À HAUTE PURETÉ

par

G. A. Kent*

RÉSUMÉ

Ces recherches ont été exécutées dans le but de produire de la giobertite (carbonate de magnésium), ou de la magnésie, contenant très peu de fer. Les traitements par flottation et séparation magnétique du minerai de giobertite non calciné ont donné des concentrés contenant 2 p. 100 de Fe (sous forme de Fe_2O_3) et 0.5 p. 100 de SiO_2 . Les traitements par calcination des concentrés, suivie de flottation et de séparation magnétique, ont réduit encore la teneur en fer jusqu'à environ 1 p. 100 de Fe_2O_3 et celle de la silice jusqu'à 0.4 p. 100. Le traitement du minerai calciné ou du concentré par lixiviation à l'acide acétique dilué a donné de la magnésie contenant moins de 0.01 p. 100 de Fe_2O_3 et très peu de silice. L'auteur indique une méthode de production de magnésie à haute pureté.

*Agent scientifique senior, Section de l'usinage des minéraux industriels, Division du traitement des minéraux, Direction des mines, ministère des Mines et des Relevés techniques, Ottawa, Canada.

CONTENTS

	<u>Page</u>
Abstract	1
Résumé	ii
Introduction.....	1
Experimental.....	1
Preliminary Observations	1
Magnesite Concentrate	2
a) Experiment 1.....	2
b) Experiment 2.....	5
c) Experiment 3.....	6
d) Experiment 4.....	6
Magnesite Ores	6
Limestone	6
Observations and Discussion.....	8
Magnesite Concentrate	8
Magnesite Ore.....	9
Limestone	9
Conclusions	10
Application for Patent.....	10
Acknowledgement.....	10
Appendix: A Suggested Procedure for the Recovery of Low-Iron Magnesia from Magnesite.....	11

TABLES

<u>No.</u>		<u>Page</u>
1.	Analysis of Magnesite Concentrate and Ores and of Limestone	3
2.	Calcination and Acetic Acid Leaching Results...	3
3.	Analyses of Acetic Acid Insoluble from Magnesite Concentrates	4
4.	Analysis of MgO from Magnesite Concentrate and Ores	5
5.	Calcination and Acetic Acid Leaching Results for Limestone	7
6.	Analysis of Purified Limestone	7

= =

INTRODUCTION

A process development investigation, recently completed by the Industrial Minerals Milling Section, showed that products in the order of 2% Fe(as Fe_2O_3) and 0.5% SiO_2 could be made from a magnesite ore without calcination. Calcination of this product, followed by magnetic separation and flotation, further reduced the Fe_2O_3 and SiO_2 to about 1% and 0.4% respectively, calculated on the uncalcined basis. It was thought that even further reduction could be made by leaching the calcined material.

Magnesite ore and concentrates react slowly with dilute (1:3) hydrochloric acid. To determine the acid-soluble fraction, it is necessary to boil the sample and digest it just under boiling for several hours. Calcined concentrate reacts very quickly with the acid; however, the mixture must be digested for a while to allow the insoluble portion to settle and be easily filterable.

Because the magnesia is in an "activated" state when calcined below the dead-burned temperature, it should be possible to dissolve it with a weak acid that would not attack the iron oxide, silica or silicates. Dilute inorganic acids would attack the iron, and also give salts that would be more difficult to decompose, whereas weak organic acids that form soluble magnesium salts would decompose to magnesia upon ignition and, if iron was not attacked, would yield a pure product. Acetic acid forms very soluble magnesium acetate and should not dissolve iron oxide or silica; it is readily available in quantity and is one of the least expensive of the organic acids.

Preliminary trials using acetic acid were sufficiently successful to warrant a more thorough exploration. The results led to an application for a patent on the process, early in 1965.

EXPERIMENTAL

Preliminary Observations

To determine whether or not a separation could be made, preliminary work was done on some magnesite concentrate that had been

calcined at 1600° F in another laboratory. Two-gram samples were transferred to 250-ml beakers and 100 ml of water and 5 ml of glacial acetic acid were added. No reaction was observed. The beakers were heated, and stirred occasionally with a thermometer. Settling began at about 63° C and was rapid at about 70° C. The addition of 0.1% Separan 2610 did not appear to have any effect on coagulation. Filtration through S & S No. 589 Blue Ribbon or White Ribbon filter paper was fairly fast and the residue could be washed with cold water.

An attempt to recover $MgCO_3$ in the filtrate by adding a solution of Na_2CO_3 was not successful, due to the nature of the precipitate. The $MgCO_3$ obtained was bulky, gelatinous, and difficult to filter and wash. While conditions might be found to make a recovery in this way, no further work was done. If such a separation could be made, sodium acetate would be a by-product with a possible market value.

The acetic-acid filtrate was evaporated to dryness in a platinum dish and ignited slowly in a muffle furnace. Charring began at about 300° C and at 500° C the product was still grey. Ignition to 1000° C gave a white material, which increased in weight rapidly on exposure to the atmosphere. This material weighed about 86% of the original. The insoluble residue was determined to be mainly Fe as Fe_2O_3 and about 3.5% MgO , calculated on the original sample.

Magnesite Concentrate

a) Experiment 1

A quantity of magnesite flotation concentrate was obtained which contained 2.72% Fe as Fe_2O_3 , 0.47% Si as SiO_2 , and 46.3% Mg as MgO . (Table 1)

A twenty-gram portion of this concentrate was heated to 900° C in a weighed platinum dish. The dish and calcined product were cooled in a desiccator charged with Drierite and then weighed quickly. The loss on ignition (L. O. I.) is given in Table 2.

TABLE 1

Analysis of Magnesite Concentrate and Ores and of Limestone
(Values are given as percentage)

Determination	Flotation Concentrate	Ore No. 1	Ore No. 2	Limestone
Soluble in hydrochloric acid (1:3)		61.97	46.37	94.35
Acid-soluble Fe as Fe ₂ O ₃		2.43	4.54	0.24
Total Fe as Fe ₂ O ₃	2.72	4.75	9.06	0.52
Total Si as SiO ₂	0.47	28.54	32.01	4.49
Acid-soluble Mg as MgO		27.50	18.66	0.61
Total Mg as MgO	46.30	33.53	33.35	0.75
Acid-soluble Ca as CaO		0.02	0.11	50.64
Total Ca as CaO				51.14

TABLE 2

Calcination and Acetic Acid Leaching Results

Material	Magnesite Concentrate				Magnesite Ores	
	1	2	3	4	Ore No. 1	Ore No. 2
L.O.I. at 900° C (%)	50.72	50.71	50.74	50.75	31.60	23.13
Acetic Acid Soluble (%)	43.90	44.52	44.99	42.55	25.18	16.50
Acetic Acid Insoluble (%)	5.38	4.33	4.30	6.67	43.13	60.23

The ignited material was transferred to a 600-ml beaker and treated with 400 ml of water and 25 ml of acetic acid. The mixture was heated on a hot plate, the temperature of which was just below 100° C, and occasionally stirred with a thermometer. At about 70° C the residue coagulated and settled fairly rapidly.

The solution was filtered through an S & S No. 589 White Ribbon filter paper, giving a clear colourless filtrate. Washing with warm 1% acetic acid caused some of the residue to pass through the paper, and the resulting solution became deep yellow. When cold water was used, colourless washings were obtained. The paper and residue (see below) were placed in a tared platinum crucible, ignited at 1000° C, cooled, and weighed. Proportions of different fractions are shown in Table 2, and the compositions of residues are given in Table 3.

TABLE 3

Analyses of Acetic Acid Insoluble from Magnesite Concentrates

Determination	Exp. No. 1		Exp. No. 2		Exp. No. 3	
	A *	B **	A	B	A	B
Total Si as SiO ₂ (%)	9.30	0.50	12.04	0.52	11.58	0.50
Total Mg as MgO (%)	35.95	1.94	19.56	0.08	19.45	0.08
Total Fe as Fe ₂ O ₃ (%)	50.34	2.72	62.39	2.70	62.83	2.70
Total Mn as MnO (%)			2.37	0.10	2.39	0.10

* A % of insoluble. ** B % of original concentrate.

The acetic acid solution was evaporated below 100° C in a beaker. In a short time a small amount of reddish material precipitated, which was filtered off and added to the above residue. Evaporation was continued to a small volume and then the solution transferred to a weighed 100 ml platinum dish, where it was evaporated to a syrupy constituency. The crust that formed was broken with a platinum rod and the mass was stirred from time to time until dry. The dish was placed in an oven, at 105-110° C, overnight.

The dish and contents were placed in a muffle furnace and heated slowly to 900° C. From time to time the dish was removed, the contents stirred, and the lumps broken up. Finally the sample was ignited at 1000° C, cooled over Drierite, and weighed quickly. The proportions of acid-soluble material are recorded in Table 2. The product was white. It was analysed for L.O.I., iron, silicon, magnesium, and calcium. L.O.I. was measured at 1000° C. Iron was determined colorimetrically with o-phenanthroline and reported as Fe₂O₃. Silicon was also done colorimetrically as reduced silico-molybdate and reported as SiO₂. Magnesium was determined by EDTA titration, and calcium by flame photometry, being reported as MgO and CaO respectively. The analyses are given in Table 4.

TABLE 4

Analysis of MgO from Magnesite Concentrate and Ores
(Values given as percentages)

Material	Concentrates				Ores	
	1	2	3	4	No. 1	No. 2
Experiment No.						
L.O.I. at 1000° C	1.10	0.84	0.84	0.52	0.38	0.50
Total Fe as Fe ₂ O ₃	0.0030	0.0015	0.0059	0.0025	0.0014	0.0044
Total Si as SiO ₂	< 0.1	< 0.1	< 0.1	0.026	0.184	1.00
Total Ca as CaO	0.46	0.46	0.46			
Total Mg as MgO	98.15	97.96	98.00	98.31	98.55	97.25
Corrected for L.O.I.	99.24	98.79	98.83	98.82	98.92	97.74
Acetic Acid Soluble Mg, as MgO	43.57	43.98	44.46	42.05	24.91	16.13
% Recovery	94.1	95.0	96.0	90.8	90.6	86.4

b) Experiment 2

Twenty grams of the same concentrate was calcined as in Experiment 1, and treated with 200 ml of water and 28 ml of acetic acid. The slurry was digested at 70° C and filtered, the filtrate being yellow. Filtering was discontinued after the first 10-15 ml and the volume of the slurry increased to about 325 ml. Digestion and filtration were repeated, yielding a pale yellow filtrate. The cold-water washings were colourless.

After drying, the magnesium acetate was ignited, first over a burner, and then at 1000° C in a furnace. The residue and product were analysed as in Experiment 1, with results as shown in Tables 2, 3 and 4.

c) Experiment 3

This experiment was similar to Experiment 2, except the calcined material was treated with 400 ml of water and 30 ml of acetic acid. The results are given in Tables 2, 3 and 4.

d) Experiment 4

This experiment was the same as Experiment 1, with the acetic acid wash omitted. The residue was not analysed. Calcination and leaching results are given in Table 2, and the analyses of the product in Table 4.

Magnesite Ores

Two magnesite ores from different localities were analysed, with results shown in Table 1. Twenty-gram portions were calcined at 900° C and then treated with 400 ml of water and 15 ml of acetic acid. The procedure used in Experiment 4 was followed. Calcination and leaching results are shown in Table 2, and the analyses of the products in Table 4.

Limestone

A sample of limestone was analysed, with the results shown in Table 1. One twenty-gram portion was leached without calcination and another twenty-gram portion was calcined at 900° C before leaching. In both cases the leach solution was 400 ml of water and 25 ml of acetic acid, at a temperature of 70° C. This was followed by the procedure used in Experiment 4. Calcination and leaching results are shown in Table 5 and the analyses of the purified limestone in Table 6. Calcium and magnesium were determined by EDTA titration, iron by o-phenanthroline, and silicon by reduced silico-molybdate.

TABLE 5

Calcination and Acetic Acid Leaching Results for Limestone

Determination	Calcined	Uncalcined
L.O.I. at 900° C (%)	40.63	-
Acetic Acid Soluble (%)	52.07	46.69
Acetic Acid Insoluble (%)	7.21	12.51

TABLE 6

Analysis of Purified Limestone
(Values given as percentages)

Determination	Calcined	Uncalcined
L. O. I.	0.28	0.35
Total Fe as Fe ₂ O ₃	0.0048	0.139
Total Si as SiO ₂	0.572	0.017
Total Mg as MgO	1.41	1.46
Total Ca as CaO	96.37	97.82
Corrected for L. O. I.	96.64	98.16
Acetic acid Soluble Ca, as CaO	50.32	45.83
% Recovery	99.37	90.50

OBSERVATIONS AND DISCUSSION

Magnesite Concentrate

Magnesium carbonate begins to decompose at about 350° C, and at 900° C is completely decomposed to MgO. After calcination at 900° C and cooling, the material increases in weight rapidly on exposure to the atmosphere and must, therefore, be weighed quickly. It is also in a reactive state, for it dissolves rapidly in weak acids. Heating to above 1200° C would produce relatively inactive "dead-burned" MgO. Temperatures between 900° C and 1200° C could be used, but are not necessary for the leaching procedure, the lower temperature being the more economical.

Since the magnesia is not completely leached from the calcined material, it was thought that washing the residue with warm dilute acetic acid would increase the recovery. However, as shown in Experiment 1, this washing caused some of the residue to pass through the filter paper. In all experiments, washing with cold water gave clear, colourless washings. The volume of leach liquor is relatively large and it is possible that washing did not increase the recovery by a significant amount. If the solution could be removed almost completely from the residue, say by suction filtration, washing might not be necessary.

Decreasing the volume of leach liquor as in Experiment 3, or increasing the acid content as in Experiments 3 and 4, did not give favourable results. Coagulation and settling at 70° C were not good and the filtrates were yellow. While the recoveries might be somewhat higher, the iron in the product might also be higher. Experiments 1 and 4 indicate that a large volume of leach liquor, containing just enough acid to react with the MgO, gives a better product.

It is difficult to evaporate a solution of magnesium acetate to dryness in platinum dishes. A crust forms that must be broken often, and later the mass must be stirred and broken up. Increasing the temperature causes spattering. On a large-scale operation the syrup might be sprayed into a kiln, where the small drops would evaporate quickly, forming a fine powder that should calcine readily. The syrup might also be spray-dried in a vacuum. Neither of these procedures was attempted.

In Experiments 2 and 3 the dried magnesium acetate was ignited over a burner. The gases evolved burned with a smoky flame and considerable charring. Ignition at 1000° C produced material that was difficult to pulverize, the final product being light grey. In the other experiments, ignition to 900° C was made slowly in a furnace. The material was much softer and a white product was obtained.

Since the purified MgO increased in weight rapidly on exposure, the products were stored in glass-stoppered weighing bottles over Drierite. If a large quantity was being produced, it should be transferred while hot to a dry, CO_2 -free atmosphere.

Magnesite Ore

The leach filtrates from these ores were clear and colourless. No difficulty was encountered in igniting the acid-soluble material, and a white product was obtained.

The recoveries were somewhat lower than those for concentrates, but a low-iron product was obtained. These ores contain a large amount of silicate, which may account for the high silica values. Possibly decreasing the amount of acetic acid would give less silica in the product.

Limestone

As CaCO_3 is readily attacked by dilute acetic acid, leaching was done on both calcined and uncalcined material. The filtrate from the calcined portion was pale yellow and that from the uncalcined was almost colourless; however, upon evaporation the second filtrate turned deep yellow.

Upon evaporating to dryness the solution did not form a crust, but crept up the sides of the platinum dishes. It was necessary to add the solutions to the dishes in small portions and evaporate to dryness between each addition. No difficulty was encountered during ignition to 1000° C; the material pulverized more easily than the magnesia from the magnesite concentrate and ores. The product from the calcined material was white, the other slightly grey.

CONCLUSIONS

1. Calcination at 900° C converts magnesite to active MgO.
2. The active MgO may be leached with dilute acetic acid at 70° C, yielding an easily filterable product very low in iron and, for magnesite concentrates, also low in silica.
3. Limestone may be leached with dilute acetic acid, with or without calcination, to give a product with considerably reduced iron and silica content.

APPLICATION FOR PATENT

In January, 1965, patent procedure was initiated. A search indicated that this method had not been covered, and authorization to apply for a patent was given.

ACKNOWLEDGEMENT

The author is grateful to Mr. R. A. Wyman, Head of Industrial Minerals Milling Section, for his advice, encouragement and valuable suggestions during this investigation.

APPENDIX

A Suggested Procedure for the Recovery of Low-Iron Magnesia from Magnesite

Pulverize the magnesite ore or concentrate to -28 mesh and calcine at 900°C (1650°F). Pulp the calcined material with about 20 times its weight of water and add 1.4 lb of glacial acetic acid per pound of MgCO_3 (calculated from HCl-soluble minus soluble iron as Fe_2O_3). Heat to 70°C with stirring, and filter by suction (Note 1). Flash off most of the water and evaporate to a thin syrup. Spray this syrup into the cold end of a kiln (Note 2) that contains an oxidizing atmosphere, is about 1000°C at the hot end, and is of sufficient length to ensure complete removal of carbon formed by the decomposition of magnesium acetate. The magnesia should be stored in a dry, CO_2 -free atmosphere; for example, in tightly-closed, fully packed containers.

Note 1.

The filter cake should be sucked dry. If desired it could be washed with cold water, but subsequently this would have to be evaporated off. It might not be economical to recover the small amount of magnesium left in the cake.

Note 2.

The syrup could be spray-dried to yield magnesium acetate, which could be converted to any desired magnesia salt by reacting with the appropriate acid.

GAK:lh