BuMines RI 7922

Report of Investigations 7922

Steam Pyrohydrolysis of Hydrous Magnesium Chlorides

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MARCH 3, 1849

UNITED STATES DEPARTMENT OF THE INTERIOR
Rogers C. B. Morton, Secretary

BUREAU OF MINES
Thomas V. Falkie, Director

BIBLIOGRAPHIC DATA SHEET

1. Report No.
BuMines RI 7922

2.

PB 234 686

4. Title and Subtitle
Steam Pyrohydrolysis of Hydrous Magnesium Chlorides

5. Report Date
July 1974

6. Performing Organization Code

7. Author(s)
John L. Reuss and Joan T. May

8. Performing Organization Rept. No.

9. Performing Organization Name and Address
Salt Lake City Metallurgy Research Center
Bureau of Mines, USDI
1600 East 1st South Street
Salt Lake City, UT 84112

10. Project/Task/Work Unit No.

11. Contract/Grant No.

12. Sponsoring Agency Name and Address
Office of Assistant Director--Metallurgy
Bureau of Mines
U.S. Department of the Interior
Washington, DC 20240

13. Type of Report & Period Covered
Research, FY 1971-74

14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstracts

A laboratory study was conducted to investigate the technical feasibility of decomposing hydrous magnesium chlorides by means of a steam pyrohydrolysis technique. This procedure consisted of injecting steam into the atmosphere of a decomposition furnace containing samples of hydrous magnesium chloride and determining the rate of hydrolysis by measuring the rate of chloride evolution. The variables investigated were temperature, amount of water vapor in the decomposition atmosphere, and hydration stage of magnesium chloride. The application of steam was shown to accelerate both the rate and completeness of magnesium chloride decomposition reactions. For example, when magnesium chloride hexahydrate is exposed to a furnace temperature of 600° C in an air atmosphere for 20 minutes, the decomposition is 37 percent. Under identical conditions in a steam atmosphere, the decomposition is in excess of 70 percent. The magnesium oxide produced by the steam pyrohydrolysis of magnesium chloride dihydrate at 800° C contained 98 percent magnesium oxide. Based on magnesium oxide composition, this is equivalent to that of burned magnesite produced at temperatures in excess of 1,300° C. In addition, to demonstrate the quality of the product on a practical basis, metal reduction tests have shown it to be equivalent to reagent grade magnesium oxide as a carbothermic reduction feed material.

17. Key Words and Document Analysis 17a. Descriptors

Metallurgy
  Chemical reactions, oxidation 0704
  Magnesium oxides 0702
  Magnesium chlorides 0702
  Metallurgical furnaces 1309 1301

17b. Identifiers/Open-Ended Terms

17c. COSATI Field/Group

07 Chemistry	A. Chemical Engineering
07 Chemistry	B. Inorganic Chemistry
11 Materials	F. Metallurgy

18. Distribution Statement
Release unlimited by NTIS.

19. Security Class (This Report)
UNCLASSIFIED

20. Security Class (This Page)
UNCLASSIFIED

21. No. of Pages
14

22. Price
3.00 — 1.45

CONTENTS

ILLUSTRATIONS

TABLES

STEAM PYROHYDROLYSIS OF HYDROUS MAGNESIUM CHLORIDES

by

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ABSTRACT

A laboratory study was conducted by the Bureau of Mines to investigate the technical feasibility of decomposing hydrous magnesium chlorides by using a steam pyrohydrolysis technique. This procedure consisted of injecting steam into the atmosphere of a decomposition furnace containing samples of hydrous magnesium chloride and determining the rate of hydrolysis by measuring the rate of chloride evolution. The variables investigated were temperature, amount of water vapor in the decomposition atmosphere, and hydration stage of magnesium chloride.

The application of steam was shown to accelerate both the rate and completeness of magnesium chloride decomposition reactions. For example, when magnesium chloride hexahydrate is exposed to a furnace temperature of 600° C in an air atmosphere for 20 minutes, the decomposition is 37 percent. Under identical conditions in a steam atmosphere, the decomposition is in excess of 70 percent. The magnesium oxide produced by the steam pyrohydrolysis of magnesium chloride dihydrate at 800° C contained 98 percent magnesium oxide. Based on magnesium oxide composition, this is equivalent to that of burned magnesite produced at temperatures in excess of 1,300° C. To demonstrate the quality of the product on a practical basis, metal reduction tests have shown it to be equivalent to reagent-grade magnesium oxide as a carbothermic reduction feed material.

INTRODUCTION

The production of magnesium from brines of the Great Salt Lake has commenced. NL Industries has completed construction of a magnesium extraction and electrolytic metal production facility with a design capacity of 45,000 tons of magnesium metal annually (<u>11</u>).[3] Also, the Great Salt Lake Minerals and Chemical Corp. has recently completed construction of a facility with a

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[1] Project leader.

[2] Research chemist.

[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

planned annual production capacity of 600,000 tons of magnesium chloride hexahydrate (8).

Because of the availability of magnesium chloride hexahydrate production facilities and information developed during prior research conducted at the Salt Lake City Metallurgy Research Center, which indicated that magnesium chloride hexahydrate exhibits a strong tendency to decompose at relatively moderate temperatures (7), a laboratory investigation was initiated to determine its suitability as a source of magnesium oxide. The purpose of this Bureau of Mines investigation was to determine the technical feasibility of producing from magnesium chloride hexahydrate a high-purity magnesium oxide, which would be competitive with dead-burned magnesite as a refractory product or as a carbothermic reduction feed material.

As a means of evaluating the quality of the magnesium chloride decomposition residue on a practical basis, it was subjected to a carbothermic reduction test. In the carbothermic reduction of magnesium oxide to magnesium metal, the presence of small quantities of impurities have a measurable effect on magnesium recovery and conversion efficiency (4). Consequently, the comparison of magnesium chloride decomposition residue and reagent-grade magnesium oxide as carbothermic reduction feed materials provided an attractive method of product evaluation.

Magnesium oxide is produced commercially in a number of different grades intended for various specific purposes (3), generally by calcining selected grades of magnesite or seawater magnesium hydroxide. Magnesium oxide has also been produced by decomposing hydrated magnesium chlorides obtained as a byproduct from the potash mineral industry (2).

Pure magnesium oxide has a sintering temperature in excess of 2,000° C, but the presence of certain impurities, particularly ferric oxide, lowers the sintering temperature considerably. Most natural magnesites contain sufficient impurities to yield a refractory-grade magnesia product by calcining at temperatures of approximately 1,400° C. Relatively pure grades of magnesium hydroxide obtained by precipitation from seawater require the addition of between 2 and 7 percent ferric oxide to permit fluxing, and recrystallization at the maximum temperature of an oil- or gas-fired rotary kiln (6, p. 726).

High-purity magnesium oxide has been produced by the thermal decomposition of hydrated magnesium chlorides. A commercial plant, designed to process the hydrated magnesium chlorides available as a byproduct from potash mineral beneficiation, operated between 1955 and 1961 (2). This plant utilized a process that consisted of (1) separating the magnesium chloride from the potassium brine circuits, (2) concentrating the magnesium chloride brines by evaporation, (3) drying the concentrated brines to produce magnesium chloride dihydrate, (4) calcining the dihydrate at 550° to 600° C to produce a material containing 80 percent magnesium oxide (MgO) and 12 percent magnesium sulfate ($MgSO_4$), and (5) calcining at 1,500° C to decompose the $MgSO_4$ and volatilize the remaining alkali chlorides.

A major disadvantage of all the known techniques for the production of refractory-grade magnesium oxide products is that they are required to operate calcination furnaces at temperatures in excess of 1,400° C (6). These temperatures are required to decompose the currently used feed materials of magnesite, magnesium hydroxide, and hydrated magnesium chlorides.

Laboratory investigations have shown that, when magnesium chloride hexahydrate is heated, the reactions occurring within the temperature range from 95° to 900° C are believed to correspond to the following equations as shown in table 1 (1, 5-7, 9). The equations shown for steps 1, 2, and 3 are believed to occur sequentially at the temperatures indicated, but at temperatures above 240° C, where reactions 4, 5, and 6 predominate, specific decomposition temperatures are not available.

TABLE 1. - Stepwise decomposition of $MgCl_2 \cdot 6H_2O$

Step	Temperature range, ° C	Reaction
1a	95-117	$MgCl_2 \cdot 6H_2O \longrightarrow MgCl_2 \cdot 4H_2O + 2H_2O$
1b		$MgCl_2 \cdot 6H_2O \longrightarrow MgOHCl + HCl + 5H_2O$
2a	135-182	$MgCl_2 \cdot 4H_2O \longrightarrow MgCl_2 \cdot 2H_2O + 2H_2O$
2b		$MgCl_2 \cdot 4H_2O \longrightarrow MgOHCl + HCl + 3H_2O$
3a	185-240	$MgCl_2 \cdot 2H_2O \longrightarrow MgCl_2 \cdot H_2O + H_2O$
3b		$MgCl_2 \cdot 2H_2O \longrightarrow MgOHCl + HCl + H_2O$
4a	+240	$MgCl_2 \cdot H_2O \longrightarrow MgCl_2 + H_2O$
4b		$MgCl_2 \cdot H_2O \longrightarrow MgOHCl + HCl$
5	+240	$MgOHCl \longrightarrow MgO + HCl$
6	+240	$MgCl_2 + H_2O \longrightarrow MgO + 2HCl$

RAW MATERIALS

Only two raw materials, analytical reagent-grade magnesium chloride hexahydrate and commercial-grade magnesium chloride dihydrate, were used in this investigation. The commercial-grade magnesium chloride dihydrate ($MgCl_2 \cdot 2H_2O$) was supplied by the Dow Chemical Co.,[4] Texas Div., Freeport, Tex. The chemical compositions of these raw materials are presented for comparison in table 2.

TABLE 2. - Chemical composition of raw materials, percent

Raw materials	Mg	MgO	Cl	H_2O
$MgCl_2 \cdot 6H_2O$......................	12.0	-	34.9	53.1
$MgCl_2 \cdot 2H_2O$......................	19.0	1.7	52.3	26.5

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[4] Reference to specific equipment is made for identification only and does not imply endorsement by the Bureau of Mines.

EQUIPMENT AND PROCEDURE

The pyrohydrolysis apparatus consisted of a (1) 3-inch-diameter combustion-tube electric furnace with associated temperature-measuring and controlling equipment, (2) a flowmeter to control air input, (3) a positive displacement metering pump and heated vaporizing flask to generate and maintain a desired steam input, (4) a sealed ceramic combustion tube with required entrance and exit ports, (5) and an exhaust gas scrubber system. This apparatus is shown schematically in figure 1.

The general test procedure consisted of charging a Vycor boat containing 50 grams of hydrated magnesium chloride into the combustion-tube furnace that had been heated to a preselected temperature between 200° and 800° C. The sample was permitted to remain in the furnace for 100 minutes; and air, steam, or a mixture of air and steam was used to sweep the gaseous decomposition products out of the combustion tube. When air was employed, the sweep gas input rate was maintained at 3.5 liters per minute. When steam alone was used, the rate of steam injection was 4.0 grams per minute. When air and steam were used, the sweep gas input rate was maintained at 3.5 liters per minute and

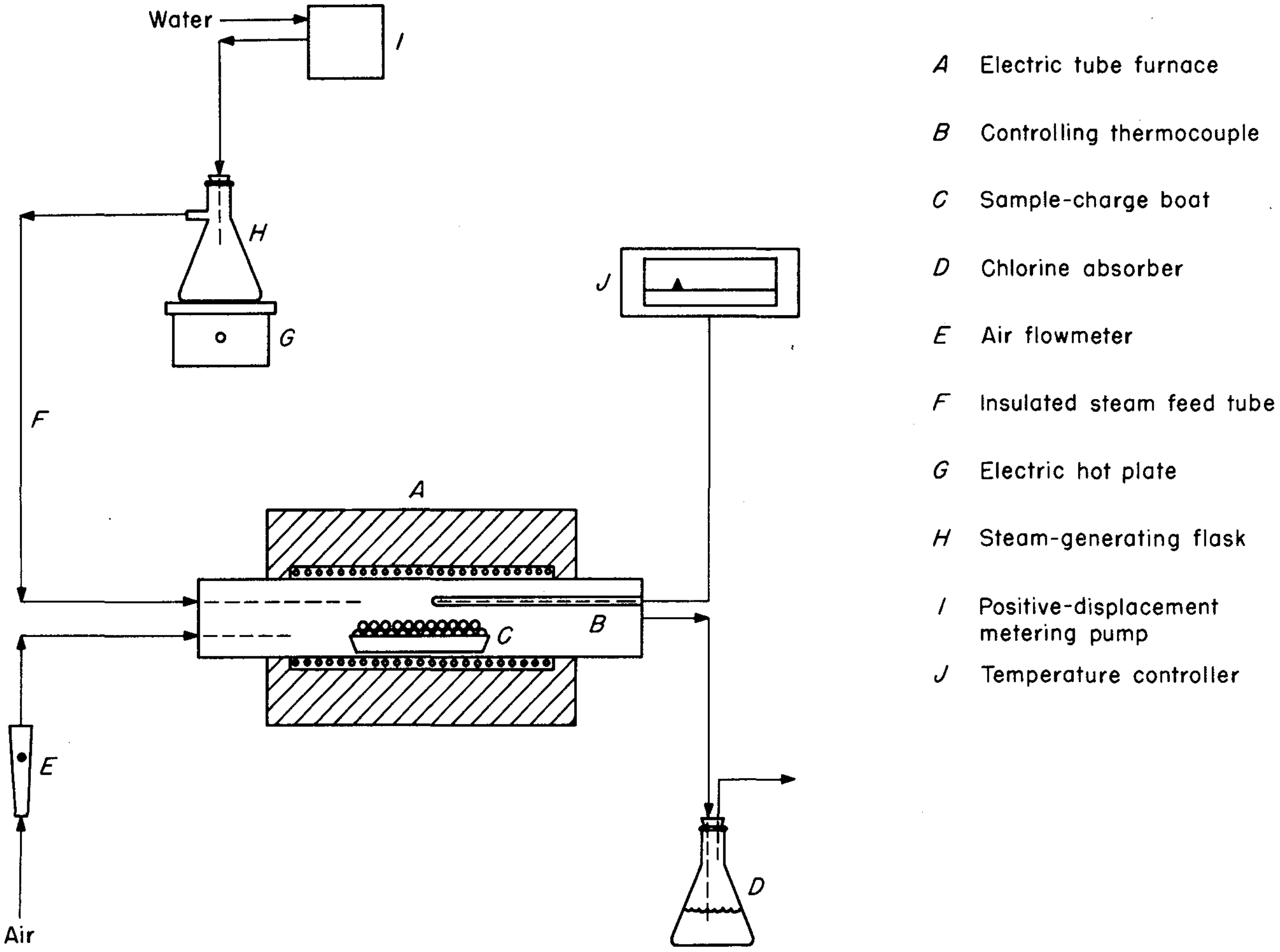

FIGURE 1. - Schematic diagram of pyrohydrolysis apparatus.

delivered 1.0 gram per minute of water to the furnace atmosphere. Samples produced for subsequent carbothermic reduction evaluations were obtained by the steam pyrohydrolysis of magnesium chloride dihydrate at 800° C with a steam-to-solid feed ratio of 1.5 to 1.0. The pressure within the combustion tube did not exceed 1 inch of water gage pressure.

The rate of hydrolysis was determined by measuring the rate at which chloride was evolved from the sample. This was accomplished by directing the furnace exhaust gas through a flask containing a sodium hydroxide solution. These flasks were removed from the exhaust line at 5- to 15-minute intervals during the test. Following completion of the test, the flasks were weighed and the solutions analyzed for chloride. The cumulative weight of chloride was then plotted against time.

RESULTS

Pyrohydrolysis of Magnesium Chloride Hexahydrate

The pyrohydrolysis of magnesium chloride hexahydrate was investigated at temperatures between 200° and 700° C in the presence of air and steam atmospheres. Because magnesium chloride hexahydrate melts in its own water of hydration at 105° to 115° C, decomposition occurs rapidly until solidification

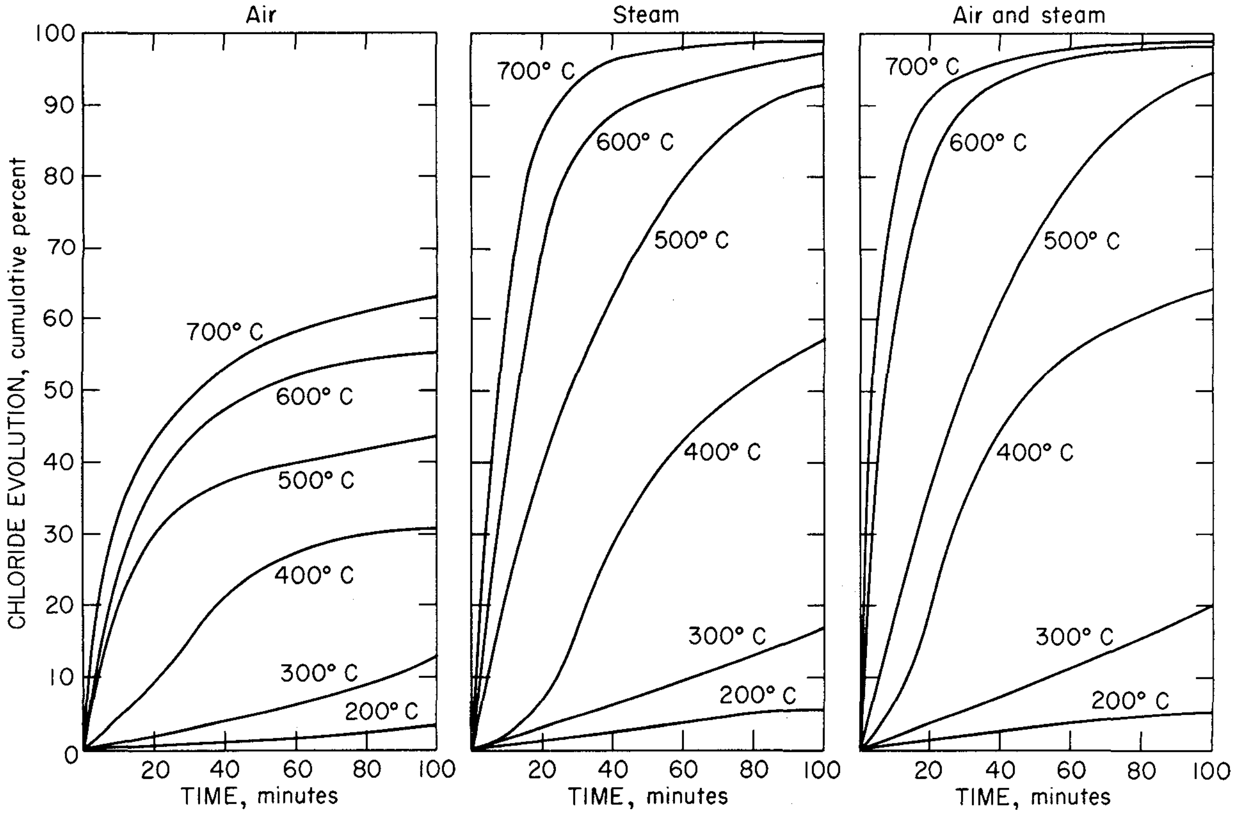

FIGURE 2. - Effect of temperature and steam on removal of chloride from $MgCl_2 \cdot 6H_2O$.

occurs. This rapid decomposition is desirable; however, the liquid phase presents potential processing difficulties in the design and operation of a commercial decomposition furnace. The results of this investigation (fig. 2) indicate that pyrohydrolysis is considerably enhanced by the introduction of steam. The runs with steam alone were made at a steam-to-solids ratio of 8 to 1 and those with air and steam at a ratio of 2 to 1.

Pyrohydrolysis of Magnesium Chloride Dihydrate

Magnesium chloride dihydrate, which does not melt below 1,000° C and is produced commercially by tray or spray drying of the hexahydrate, does not exhibit any obvious processing difficulties. Consequently, an investigation similar to that described for the decomposition of the hexahydrate was conducted using a sample of commercially produced dihydrate obtained from the Dow Chemical Co. The only deviation from the previous procedure was that the temperature range investigated was between 300° and 800° C. The results of this investigation, as given in figure 3, show that the pyrohydrolysis of magnesium chloride dihydrate is similar to that of the hexahydrate; however, it retains its solid state throughout the temperature range investigated and requires additional heat energy to obtain a comparable degree of decomposition. The runs with steam alone were made at a steam-to-solids ratio of 8 to 1, and those with air and steam at a ratio of 2 to 1.

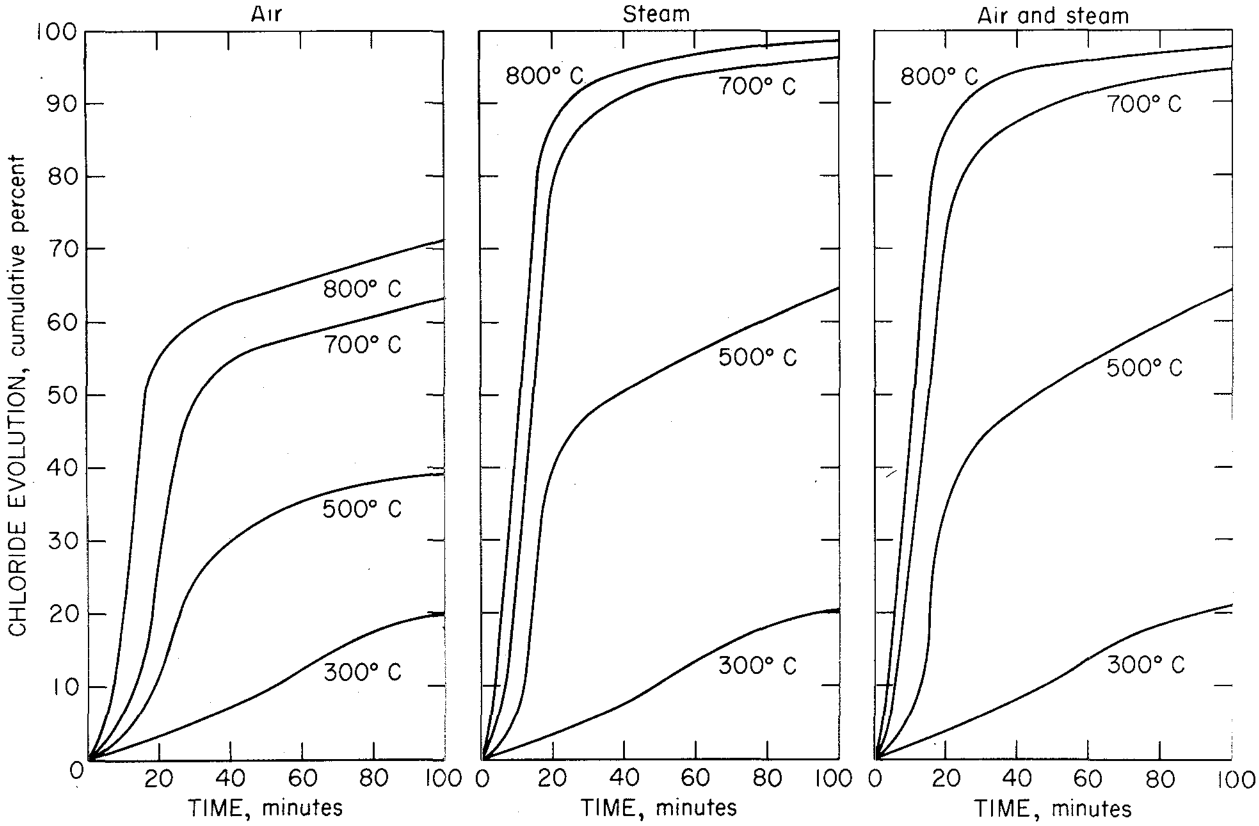

FIGURE 3. - Effect of temperature and steam on removal of chloride from $MgCl_2 \cdot 2H_2O$.

Carbothermic Reduction of Pyrohydrolysis Furnace Residue

In the carbothermic reduction method of producing magnesium metal, a high-purity magnesium oxide feed material is required to prevent corrosion of the high-temperature induction furnace and provide a reasonable metal conversion efficiency. To determine the quality of the magnesium oxide produced by the steam pyrohydrolysis technique, a batch of furnace residue, produced by the steam pyrohydrolysis of magnesium chloride dihydrate at 800° C with a steam-to-solid feed rate of 1.5 to 1.0, was evaluated as a potential feed material. Table 3 shows the results of laboratory carbothermic reduction tests comparing the pyrohydrolysis residue and reagent-grade magnesium oxide. Corrosion of the furnace from the chloride in the pyrohydrolysis residue was not evident.

TABLE 3. - Carbothermic reduction of MgO products, percent[1]

Feed material	Feed composition				Mg recovery	Conversion efficiency
	Mg	MgO	Ca	Cl		
Reagent-grade MgO........	59.5	99.2	0.03	0.005	85.3	83.6
Pyrohydrolysis residue...	58.8	98.0	.06	.30	87.8	86.1

[1] The metal produced from each of the feed materials contained in excess of 99 percent magnesium.

DISCUSSION OF RESULTS

Predictably, the thermal decomposition of hydrous magnesium chloride, which is a hydrolysis-type reaction, was accelerated by the introduction of steam to the decomposition furnace atmosphere. The increased availability of water would be expected to drive the hydrolysis reaction more nearly to completion. The availability of abundant internal water is probably responsible for the strong tendency of hydrous magnesium chlorides to decompose in the lower hydration stages. Apparently, the presence of steam in the decomposition furnace atmosphere introduces external water vapor, which can either diffuse into the sample or, because of its saturation of the atmosphere in contact with the sample, inhibit the release of internal water from the sample. Each of these conditions makes water available to hydrolyze the magnesium chloride into magnesium oxide and hydrogen chloride.

The decomposition rate of magnesium chloride hexahydrate is very rapid during its initial 10-minute exposure to the steam environment of the decomposition furnace. This rapid decomposition probably occurs because of the following: (1) A large excess of internal water is available within the crystal structure; and (2) because magnesium chloride hexahydrate melts in its own water of hydration at 105° to 115° C, decomposition occurs rapidly until solidification. This rapid decomposition is desirable; however, the formation of a fluid liquid phase presents potential processing difficulties in the design of a commercial decomposition furnace.

The initial rate of decomposition of the magnesium chloride dihydrate is not as rapid as that obtained with the hexahydrate. This is to be expected because the dihydrate contains less internal water and does not melt below 1,000° C. The advantage of the dihydrate is that it retains its solid state throughout the decomposition temperature range and does not exhibit any obvious processing difficulties. To obtain a degree of decomposition comparable with that obtained with the hexahydrate at 700° C, it is necessary to heat the dihydrate to 800° C.

In this study, an attempt was made to evaluate the influence of steam concentration on the pyrohydrolytic decomposition of hydrous magnesium chlorides. Steam-to-feed ratios of 2 to 1 and 8 to 1 were evaluated with both magnesium chloride hexahydrate and magnesium chloride dihydrate with comparable results. The optimum amount of steam required will vary with the type of feed, furnace design, furnace temperature, and furnace residence time; however, the results of this investigation indicated that steam-to-feed weight ratios in excess of 2 to 1 were superfluous.

The magnesium oxide produced by the pyrohydrolysis of commercial-grade magnesium chloride dihydrate is less pure than reagent-grade magnesium oxide on a magnesium oxide content basis. However, based on magnesium recovery, conversion efficiency, and metal composition obtained from metal reduction tests in the laboratory, it has been shown to be equivalent to reagent-grade magnesium oxide as a carbothermic feed material. The quality of this magnesium oxide has not been evaluated with respect to its application as a refractory material; however, its magnesium oxide content is equivalent to that of burned magnesite (10).

CONCLUSIONS

A laboratory study was conducted to study the technical feasibility of decomposing hydrous magnesium chlorides by means of a steam pyrohydrolysis technique. The results of this investigation, based on chloride evolution, chemical analysis of furnace residue, and conversion of furnace residue to magnesium metal by the carbothermic reduction method, indicated the following:

1. The application of steam accelerates both the rate and completeness of hydrous magnesium chloride decomposition reactions.

2. The magnesium oxide produced by the pyrohydrolytic decomposition of hydrous magnesium chlorides appears suitable for use as a refractory or for direct reduction to metal.

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INT.-BU.OF MINES,PGH.,PA. 19443