Oxides in the Dehydration of Magnesium Chloride Hexahydrate

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In the name of God

To my parents and my dear wife

Abstract.

A novel and accurate method of chemical analysis was developed to identify and assay the products of the hydrolysis that occurred when magnesium chloride hexahydrate was heated and held at temperature and reacted with its own liberated waters of hydration. The novel method took advantage of the solubility of magnesium chloride and magnesium chloride hydrates in methanol and the concomitant insolubility of magnesium oxide and magnesium hydroxychlorides in methanol. The method was found to have a precision of 5-7 % and represents a substantial improvement over previous analytical methods. The method is also readily applied to any methanol soluble salt containing insoluble impurities, meaning that it can also be used for the monitoring of the fused salt electrolyte present the magnesium electrolysis cells.

Experiments were performed to study the composition and the extent of formation and transformation of the non-equilibrium products of dehydration and hydrolysis of $MgCl_2.6H_2O$ (bischofite). One gram bischofite samples were held at temperature for varying times under uncontrolled atmospheres in the temperature range from 200 to 600 ^oC. Using the present method of analysis, the oxide that was initially formed during dewatering and hydrolysis was found to be poorly crystalline magnesium hydroxychloride for all dehydration temperatures other than 600 ^cC where it also contained some MgO.

Upon holding at temperature, it was found that the dewatering and hydrolysis continued to occur gradually at temperatures up to 400 ^oC and that the amount of the magnesium hydroxychloride formed from the ongoing hydrolysis increased with holding time. By contrast, the mass of magnesium hydroxychloride produced by holding at 500 and 600 ^oC peaked at around 60 seconds of holding and suggested that there was an initial very rapid 'rearrangement' of the Mg, Cl, H and O atoms to produce the poorly crystalline magnesium hydroxychloride phase. It is believed that this '*primary*' hydrolysis occurs to some extent to produce the initial, poorly crystalline magnesium hydroxychloride that was detected at the end of the heating to any temperature.

The novel analytical method provided the ability to identify, and thus prepare, various forms of hydroxychlorides thereby facilitating the examination of the thermal decomposition kinetics of two magnesium hydroxychlorides, namely, MgOHCl and $Mg_2(OH)_3Cl.2H_2O$. For the former, it was found that the decomposition of MgOHCl commenced at 376 ^{o}C and it directly converted into MgO and HCl without undergoing any intermediate step. For the latter, thermogravimetric Analysis (TGA) showed that the decomposition of $Mg_2(OH)_3Cl.2H_2O$ exhibited a single intermediate stage wherein crystalline water was lost at roughly 108 ^{o}C. Conversion of the resulting $Mg_2(OH)_3Cl$ to MgO, HCl and H_2O occurred at temperatures above 398 ^{o}C.

The present research provides insight to the challenge of minimizing magnesium oxide and magnesium hydroxychloride during the preparation of feed for the electrolytic production of magnesium because it shows the virtually unavoidable tendency of rapid hydrolysis to occur due to the local water vapour pressure that is created during the tonnage processing of material. Armed with the present findings and supported by the novel analytical technique, future researchers will be better able to undertake the task of improving the performance of existing operations for the preparation of feed for electrolytic magnesium production and be able to explore and develop novel, and it is believed simpler, methods for the production of anhydrous magnesium chloride on a commercial scale.

Résumé

Une nouvelle méthode d'analyse chimique a été développée pour identifier et tester les produits d'hydrolyse qui se forment quand le chlorure de magnésium hexahydrate est chauffé, maintenu à température constante et qu'il réagit avec les eaux d'hydratation qu'il libère. La nouvelle méthode tire avantage de la solubilité du chlorure de magnésium, hydraté ou non, et en parallèle de l'insolubilité de l'oxyde et des hydroxychlorures de magnésium dans le méthanol. Il s'avère que la méthode a montré une précision de 5-7 %, ce qui apporte une importante amélioration aux méthodes analytiques précédentes. La méthode est aussi facilement applicable a tout sel soluble, qui contiendrait des impuretés insolubles, dans le méthanol, ce qui signifie qu'elle peut aussi être utilisée pour le suivi de l'électrolyse de sel fondu présent dans les cellules d'électrolyse du magnésium.

Les expériences ont été réalisées pour étudier la composition, et le degré de formation et de transformation, des produits non-équilibrés de déshydratation et d'hydrolyse de $MgCl \cdot 6H_2O$ (*Bischofite*). Des échantillons de un gramme de *Bischofite* ont été maintenus à des températures constantes, dans une gamme de températures de 200 à 600 °C, pendant des durées variables, sous atmosphère ambiante. En utilisant cette nouvelle méthode d'analyse, il a été montré que le premier oxyde formé au cours de la déshydratation et de l'hydrolyse est un hydroxychlorure de magnésium mal cristallisé pour toute température de déshydratation autre que 600 °C, température à laquelle du MgO est aussi présent.

En maintenant la température constante, il a été observé que la déshydratation et l'hydrolyse se poursuivent progressivement jusqu'à 400 °C et que la quantité d'hydroxychlorure de magnésium formé au cours de l'hydrolyse augmente avec le temps de réaction. En revanche, la masse d'hydroxychlorure de magnésium produite à 500 et 600 °C atteint un maximum après environ 60 secondes, suggérant un 'réarrangement' précoce très rapide des atomes de Mg, Cl, H et O produisant ainsi la phase d'hydroxychlorure de magnésium mal cristallisé. Cette hydrolyse '*primaire*' semble être à l'origine, dans une certaine mesure, de la production précoce de l'hydroxychlorure de magnésium mal cristallisé qui fut détecté à la fin des tests à toutes les températures.

La nouvelle méthode analytique a permis d'identifier, et donc de préparer, différentes formes d'hydroxychlorures, facilitant ainsi l'étude de la cinétique de décomposition thermique de deux hydroxychlorures de magnésium, plus précisément MgOHCl et $Mg_2(OH)_3Cl{\cdot}2H_2O$. Pour le premier, il a été observé que la décomposition du MgOHCl débutait à 376 °C et que ce dernier était directement converti en MgO et HCl, sans étape intermédiaire. Pour le second, l'analyse thermogravimétrique (ATG) a montré que la décomposition de $Mg_2(OH)_3Cl{\cdot}2H_2O$ s'effectuait avec une étape intermédiaire au cours de laquelle l'eau structurale du cristal est perdue à 108 °C. La conversion du $Mg_2(OH)_3Cl$ en résultant s'est faite au-dessus de 398 °C et a donné du MgO, HCl et H_2O.

Cette recherche apporte un aperçu du défi que représente la minimisation de l'oxyde et de l'hydroxychlorure de magnésium lors de la préparation de l'alimentation pour la production électrolytique du magnésium, parce qu'elle montre la tendance inévitable d'une hydrolyse rapide due à la pression vapeur locale qui se crée pendant le procédé du matériau à l'échelle de la tonne. En connaissance de cause et aidé par la nouvelle technique analytique, les chercheurs pourront à l'avenir entreprendre la tâche d'améliorer la performance des opérations existantes pour la préparation de l'alimentation de la production électrolytique du magnésium et pourront explorer et développer de nouvelles méthodes, probablement plus simples, pour la production commerciale de chlorure de magnésium anhydre.

Contribution of Authors

This thesis was prepared in accordance with 'Article C' of the guidelines concerning thesis preparation of McGill University. This article reads as follows:

1. Candidate has the option of including, as part of the thesis, the text of one of more papers submitted, or to be submitted, for publication, or the clearly duplicated test (not the prints) of one or more published papers. These texts must conform to the "Guidelines for Thesis Preparation" with respect to font size, line spacing and margin sizes and must be bound together as an integral part of the thesis. (Reprint of published papers can be included in the appendices at the end of the thesis.)

2. The thesis must be more than a collection of manuscripts. All components must be integrated into a cohesive unit with a logical progression from one chapter to the next. In order to ensure that the thesis has continuity, connection text that provide logical bridges proceeding and following each manuscript are mandatory.

3. The thesis must conform to all other requirements of the "Guideline for Thesis Preparation" in addition to the manuscripts. The thesis must include the following: a table of content: a brief abstract both in English and French: an introduction which clearly states the rational and objectives of the research: a comprehensive review of the literature (in addition to that covered in the introduction to each paper): a final conclusion and summary; a through bibliography: appendix containing an ethic certificate in the case of research involving human or animal subjects, microorganism, living cells, other biohazards and/or radioactive material.

4. As manuscripts for publication are frequently very concise documents, where appropriate, additional material must be provided (e.g., in appendices) in sufficient detail to allow a clear and precise judgment to be made of the importance and originality of the research reported in the thesis.

5. In general, when co-authored papers are included in a thesis the candidate must have made a substantial contribution to all papers included in the thesis. In addition, the candidate is required to make an explicit statement in the thesis as to who contributed to such work and to what extent. This statement should appear in a single section entitle "Contribution of Authors" as a preface to the thesis. The supervisor must attest to the accuracy of this statement at the doctoral oral defense. Since the task of the examiners is made more difficult in these cases, it is the candidate's interest to clearly specify the responsibilities of all the authors of the co-authored papers.

The following are manuscripts written by the author and were used in preparation of this thesis. The design of the experimental studies and the experiments and the associated measurements were either carried out by the author or under the author's close supervision.

1. S. Kashani-Nejad, R. Harris, "The Face of Primary Magnesium Production", Prepared for journal publication, *Chapter 2.*
2. S. Kashani-Nejad, R. Harris, "Technological review of Anhydrous Magnesium Chloride Preparation", Prepared for journal publication, *Chapter 3.*
3. S. Kashani-Nejad, K-W. Ng and R. Harris, "Novel Algorithm for Magnesium Oxides Speciation", Report of Invention, McGill University, November, 2003, *Chapter 5.*
4. S. Kashani-Nejad, K-W. Ng and R. Harris, "Oxides in the Dehydration of Magnesium Chloride Hexahydrate", to be submitted to Metallurgical Transactions B, February 2005, *Chapter 7.*
5. S. Kashani-Nejad, K-W. Ng and R. Harris, "Preparation of MgOHCl by Controlled Dehydration of $MgCl_2.6H_2O$", Metallurgical Transactions B, Volume 35B(2), April 2004, 405-406, *Chapter 8.*
6. S. Kashani-Nejad, K-W. Ng and R. Harris, "Properties of Magnesium Hydroxychloride (MgOHCl)", Metallurgical Transactions B, Volume 35B(2), April 2004, 406-408, *Chapter 9.*
7. S. Kashani-Nejad, K-W. Ng and R. Harris, "MgOHCl Thermal Decomposition Kinetics", Metallurgical Transactions B, 36B(1), February 2005, 153-157, Chapter *10.*
8. S. Kashani-Nejad, K-W. Ng and R. Harris, "$Mg_2(OH)_3Cl.2H_2O$ Thermal Decomposition Kinetics", Light Metals 2004, ed. by D. Gallienne and R. Ghomashchi, Hamilton, Ontario, August 22-25, 431-442, 2004, *Chapter 11.*

All of the manuscripts presented above are co-authored by Prof. R. Harris in his capacity as research supervisor. Manuscripts 3 to 8 include K.Wing Ng (Research Assistant in the Department of Mining, Metals and Materials Engineering, McGill University) recognizing his contribution to the analysis of results. Beyond the contributions of the co-authors mentioned here, all of the work and analysis presented in this dissertation was performed by the author.

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Nomenclature

Symbol	Description	Unit	SI Unit
A	Mole fraction in FactSage™	mole	
A	Cross-sectional area	m^2	
a_i	Activity of specie i	unit-less	
C_i	Concentration of specie i	ppm	$mole/m^3$
C_j^i	Initial concentration of specie j	ppm	$mole/m^3$
E	Electrolytic reduction potential	V	
E^o	Standard electrolytic reduction potential	V	
e^o	Standard half cell reduction potential	V	
ε	Interaction parameter	unit-less	
F	Faraday's constant (96485 c/equiv.)	c/equivalence	
$\Delta G^0_{(i)}$	Standard free energy of formation for reaction i	J/mole	
$\Delta H^0_{(i)}$	Standard enthalpy of formation for reaction i	J/mole	
M_i	Moles of specie i	mole	
MW_i	Molecular weight of specie i	g/mole	
N	Normality	equivalence/l	
n	Number of moles	mole	
Q	Volumetric flowrate	m^3/s	
R	Ideal gas constant	8.314 J/mol/K	
T	Temperature	^oC	K
t	Time	minute	second
P	Pressure	atm	Pa
P_i	Partial pressure of specie i	atm	Pa
ρ_i	Density of specie i	g/l	kg/m^3
X_i	Mole fraction of specie i	mole	
v	Velocity	m/s	
$\gamma_{(i)}$	Activity coefficient of specie i	$mole^{-1}$	
$\gamma^0_{(i)}$	Activity coefficient of species i at infinite dilution	$mole^{-1}$	
r_t	Radius of particle at time t	m	
V_t	Volume of particle at time t	m^3	
N	Number of particles		
E	Activation energy	J/mol	
k	Reaction rate constant	m/s	

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Chapter 1: Introduction

The dehydration of magnesium chloride hydrates to produce anhydrous magnesium chloride containing a minimal amount of hydrolysis products is of great importance to electrolytic magnesium production processes because of the highly detrimental effects of these oxygen- and possible hydrogen-containing compounds on the performance and productivity of the electrolysis cells. The anhydrous magnesium chloride feed used commercially is obtained by either partial or complete dehydration of aqueous magnesium chloride solutions. The control of *oxide** formation during the inadvertent hydrolysis that occurs during the dehydration process is a common challenge for the magnesium production industry.

The focus of the present thesis was to study the composition and extent of formation and transformation upon holding at temperature of the non-equilibrium products of thermal dehydration and the inadvertent and undesired hydrolysis of $MgCl_2.6H_2O$ (bischofite) under an uncontrolled atmosphere. The aim of the experiments was to help understand the commercial production of as oxide-free as possible, anhydrous magnesium chloride, $MgCl_2$.

A common obstacle encountered by researchers in the study of oxide formation during the dehydration of $MgCl_2$ hexahydrate is the lack of a reliable technique to monitor the change of oxide content in the sample as the dehydration process proceeds. Due to this reason, indirect methods were previously employed. In this research, a novel method was developed to isolate the oxide species from anhydrous or hydrated magnesium chloride and by use of this technique, useful insight was gained into the mechanism and kinetics of oxide formation during thermal dehydration of magnesium chloride hexahydrate.

The thesis consists of twelve chapters. Some are in the style of a manuscript for publication so inevitably some repetition with other chapters occurs.

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* Throughout the thesis, the terms 'oxide' and 'magnesium oxides' are used to denote the class of compounds comprising magnesium oxide, MgO, and all the magnesium hydroxychlorides and the magnesium hydroxychloride hydrates. Also, due to the time over which the publications were produced, and the evolution of language and terminology, the terms magnesium hydroxchloride and magnesium hydroxylchloride have been used interchangeably.

The thesis begins with Chapter Two, which presents a short discussion on the magnesium economy. This chapter entitled "The Face of Primary Magnesium Production" by S. Kashani-Nejad and R. Harris, prepared for journal publication.

Chapter Three presents a survey of current magnesium production processes. In particular, the production processes of hydrous and anhydrous $MgCl_2$ feed for electrolysis cells are reviewed. This chapter consists of a manuscript entitled "Technological review of Anhydrous Magnesium Chloride Preparation" by S. Kashani-Nejad and R. Harris, prepared for journal publication.

Chapter Four reviews the thermal dehydration of magnesium chloride under equilibrium conditions and through an analysis of the relevant thermochemistry suggests how to prevent hydrolysis and make electrolysis-grade, anhydrous $MgCl_2$ under equilibrium condition.

Chapter Five presents a novel method to determine the composition and amounts of magnesium oxides present in dehydrated magnesium electrolysis process feed or fused salt melts used for commercial magnesium production process electrolytes regardless of the nature of the oxide species that are present. This chapter contains a Report of Invention entitled "Novel Algorithm for Magnesium Oxides Speciation" by S. Kashani-Nejad, K-W. Ng and R. Harris filed with the McGill University Office of Technology Transfer (OTT), November 2003.

Chapter Six of the thesis describes the methodology of the experiments as well as the experimental setup. The experimental procedure is also included.

Chapter Seven presents the experiments performed to study the composition and extent of formation and transformation upon holding at temperature of the non-equilibrium products of thermal dehydration and hydrolysis of $MgCl_2.6H_2O$ (bischofite) under uncontrolled atmosphere. This chapter entitled "Oxides in the Dehydration of Magnesium Chloride Hexahydrate" by S. Kashani-Nejad, K-W. Ng and R. Harris, will be submitted to Metallurgical Transactions B.

Chapter Eight and Nine present a method for the preparation of MgOHCl samples by controlled dehydration of $MgCl_2.6H_2O$ and report two properties of MgOHCl; namely, the solubility of MgOHCl in methanol and the characteristic infrared spectrum absorption peak required for development of the speciation technique presented in Chapter Four. These chapters consist of two manuscripts entitled “Preparation of MgOHCl by Controlled Dehydration of $MgCl_2.6H_2O$” and “Properties of Magnesium Hydroxychloride (MgOHCl)” by S. Kashani-Nejad, K-W. Ng and R. Harris, published in Metallurgical Transactions B, Volume 35B(2), April 2004, 405-406 and 406-408, respectively.

Chapters Ten and Eleven describe the thermal stability of oxide species produced during the dehydration of $MgCl_2.6H_2O$ upon holding at various temperatures. These chapters consist of two manuscripts entitled “MgOHCl Thermal Decomposition Kinetics” by S. Kashani-Nejad K-W. Ng and R. Harris, Publication in the Metallurgical Transaction B, Volume 36B(1), February 2005, 153-157 and “$Mg_2(OH)_3Cl.2H_2O$ Thermal Decomposition Kinetics” which was published in the Light Metals 2004 proceeding ed. by D. Gallienne and R. Ghomashchi, Hamilton, Ontario, 431-442, August 2004.

Chapter Twelve contains the overall conclusions a statement of originality and recommendations for future work.

Chapter 2: The Face of Primary Magnesium Production

2.1: Abstract

Indications are that global magnesium metal production has entered a new era over the last few years; the impact of Chinese and CIS production on western markets being enormous. Less than two decades ago China was an importer of magnesium and world production of magnesium was about 300,000 tonnes/year. Today China is the world's largest producer and exporter and the world production is 447,000 tonnes/year. Russia and China now contribute to more than 60 % of the global market. Apart from the USA, the principal remaining sources of primary metal in the West are Canada, Israel and Brazil. The Commonwealth of Independent States (CIS) has three producers, Solikamsk and Avisma in Russia and Ust-Kamenogorsk in Kazakhstan while the total number of plants in China is estimated to be 150 to 200. The present circumstances cannot be seen as stable because the world's need of magnesium has not decreased, if anything, as aluminum production raises so will demand for magnesium. Furthermore, the U.S. has recently imposed 305 % anti-dumping duty on Chinese magnesium. Western magnesium producers and business ventures plan to add new magnesium capacity by 2010 in response to increasing magnesium demand and despite the growing share of China in the global market. This review of the magnesium business presents a snap shot of the primary magnesium world in the spring of 2004.

2.2: Introduction

In recent years there has been a sharp increase in the production of magnesium from China, which almost exclusively uses the batch Pidgeon process for the production of magnesium. The Pidgeon process is labor intensive and generates plant emissions unacceptable for the North America and Europe[1]. China's position as a significant supplier of metal has led to the closure of a number of high-cost Western producers. The remaining producers have sought trade protection from this wave of metal with the result that Chinese magnesium is now subject to anti-dumping duties (305 %) in the US market[2]. Europe has also imposed import duties on Chinese metal (63 %), but since the region is no longer producing primary metal, there is a little case for enforcing those regulations[3].

However despite this tough competition, there is still much interest in the primary production of magnesium. There are at least eight active magnesium projects in Australia and Canada and an American producer returned to full production capacity in 2003. The constant increase in magnesium demand from the automotive industry has encouraged different business ventures to work toward establishing new production capacities but these interests have faced several significant technical and financial challenges.

On the technical side, the lack of proven and accessible technologies for the production of magnesium electrolysis feed and the different chemical and physical characteristics of magnesium resources forces business ventures to develop their own feed production processes. This is a complicated task without a guaranteed outcome. It is exemplified by AMC (Australia) who negotiated a fixed price construction contract that was found impossible to fulfill with the result that the project failed after very significant expenditure[4]. There is now wide spread interest in the Russian carnallite electrolysis process[5] as a consequence of such challenges in the development of technologies to produce anhydrous magnesium chloride.

Raising money for a new magnesium project is very difficult these days. Magnesium production is an infant industry and this means that it is not widely understood by the investment community. Histories of failed attempts have also made investors very cautious and very few business ventures, even with bankable feasibility studies in hand, are being successful in finding sufficient funds to progress their projects.

This article details the present status of primary production of magnesium in the world, the trend of metal applications and the market. It provides an up to date analysis of the industry. Note that all capacities are in metric tones, mt, i.e. units of 1000 kg or tonnes/year, metric tones per annum.

2.3: China

In China, companies continue to announce planned increases in their production capacities although some have delayed previously announced plans because of the SARS outbreak, a sharp rise in fuel costs and raw material and freight restrictions. According to China's National Bureau of Statistics, China produced 336,000 tones of magnesium in 2003, a 35 % increase from 2002 production levels[1]. The total number of plants in China is estimated to be between 150 to 200, although the smaller plants are often closing because of poor market conditions[6]. Some of the Chinese expansion plans are described below.

The major Chinese magnesium producer, Shanxi Jishan Huayu plans to increase its production capacity from 20,000 tonnes/year to 40,000 tonnes/year. This increase is part of the company's plan to reach a capacity of 100,000 tonnes/year magnesium production by 2005[7,8]. Shanxi Wenxi Baiyu Magnesium Industry Co.[9] has recently increased its capacity from 6,000 to 30,000 tonnes/year[10]. Shanxi Wenxi Yinguang Magnesium Co. Ltd.[11] plans to increase its ingot production capacity from 8,000 to 14,000 tonnes/year in series of upgrades at its works in Yuncheng City, Shanxi Province[12]. Shanxi Qizhen Magnesium Corp.[13,14] recently increased its production capacity from 14,000 to 20,000 tonnes/year[1]. Ningxia Huayuan Magnesium Corp.[14] has added a further 6,000 tonnes/year smelting capacity to its plant, bringing its total smelting capacity to 14,000 tonnes/year. Shanxi Guangling Jinghua Corp.[15] increased its ingot production capacity from 10,000 to 20,000 tonnes/year to be followed by another increase to reach a production level of 40,000 tonnes/year by the end of 2005[1]. Shanxi Zhongjin Corp. plans to increase its smelting capacity to 7,000 tonnes/year by August 2004[1]. Ningxia Hyayuan Magnesium Smelter has increased its production capacity from 8,000 to 14,000 mtpy[10]. Shanxi Datong Zhongjin Magnesium Industry Co. is expected to increase its ingot production to 7,000 to 8,000 tonnes/year by August 2004[1]. Dongfang Metallurgy Enterprise Co. Ltd. plans to increase its production capacity form 11,000 to 30,000 tonnes/year. A new China-Hong Kong joint-venture, Yuxing Hongfu Magnesium Co. plans the construction of a 50,000 tonnes/year magnesium plant in Shanxi province. This plant is expected to reach full capacity by the end of 2005[10]. Shanxi Xi County Hongfu Magnesium Co. Ltd.

launched a magnesium project with the capacity of 50,000 tonnes/year in three phases. This plant is expected to reach its design capacity by August 2004. Ningxia United Magnesium Corporation will increase its smelting capacity to 4,000 tonnes/year in 2004[16]. Shanxi Reicheng Hengfa Corp. was expected to increase its magnesium ingot capacity from 4,000 to 12,000 tonnes/year by March 2004[10]. Shanxi Chenjin[7] will soon increase its production capacity from 6,000 to 9,000 mpta. Qinghai Minhe Metals Smelting Corporation in Qinghai Province, which has 7,000 tonnes/year ingot production capacities, is considering expansion[17]. Winca Magnesium (Hebi) Co. Ltd.[18], which produces 5,000 tonnes/year magnesium in its Hebi plant, plans further expansion[1]. Jishan Huayu Enterprises Group plans to increase its production form 11,000 to 32,000 tonnes/year. Minhe Magnesium Science and Technology Co., which produced 3,000 to 4,000 tonnes/year in 2003, is considering future expansion[19]. Shanxi Wenxi Xindi Magnesium Co. Ltd. produced 5000 mt of magnesium and is increasing its production output in 2004. Shanxi Tongxiang Magnesium Co. Ltd.[20], with 7,200 tonnes/year ingot production capacity and Shanxi Wenxi Hongfu Magnesium Co. Ltd.[21], with 6,000 tonnes/year capacity, are both considering expansion of their production capacities in 2004[14]. Jilin North Industrial Silicon Co. increased its combined alloy and ingot output to 12,000 tonnes/year in 2003[22]. In September 2002, Ninxia Zhonging aluminum Co. commenced operation at its 12,000 tonnes/year magnesium production plant[22].

2.4: Canada

Magnesium production capacity in Canada has decreased significantly after the Noranda's closure of the Magnola Metallurgie Inc. plant in the Spring of 2003[23,24]. Currently, Hydro Canada Corp. and Timminco Ltd. are the only producers of primary magnesium in Canada. Some magnesium projects are still being actively perused by newly established companies. Canada produced 50,000 tons of magnesium in 2003, considerably less than its 2002 production of 80,000 tons.

2.4.1: Hydro Magnesium Corporation

The magnesium production plant of Hydro Magnesium Corp.[25] in Becancour, Quebec, produces 48,000 tonnes/year magnesium from magnesite. This plant is the only primary magnesium production facility of the Norsk Company after the closure of its Porsgrunn plant in Norway[26] as a producer of primary metal. The Becancour plant uses Norsk's proprietary dehydration technology for production of granulated anhydrous magnesium chloride[27].

2.4.2: Timminco Ltd.

Timminco[28] is producer of magnesium, calcium and strontium metals and alloys using Pidgeon retorts. Timminco's plant in Haley is located approximately 100 kilometers west of Ottawa, Ontario and has a production capacity of 9,000 tonnes/year. In January 2004, Timminco Ltd. announced that it would close its Haley magnesium plant in the second half of 2004[1,29] as a result of the stronger Canadian dollar and intense competition from Chinese suppliers. However in early April, Timminco decided to delay the previously announced closure due to an unanticipated increase in demand for its high purity magnesium. The company stated that the closure would be deferred until further notice[30].

2.5: Future Plans (Canada)

2.5.1: Globex Mining Enterprises Inc.

Globex[31] is developing its Timmins-area magnesium–talc deposit, 13 km from Timmins, Ontario. Previous work has indicated the potential for production of both magnesium metal and high quality talc from the deposit. Results of a preliminary study conducted by Hatch Associates in 2001 were positive and indicated good economic returns using available technologies. The project would include a mine-mill complex located near Timmins, Ontario consisting of mining and feed preparation, flotation to remove by product minerals and impurities and upgrading of talc to a salable byproduct and calcination unit to produce MgO. The second portion of the project will be located near Rouyn-Noranda Quebec, and will consist of a large smelter complex to produce pure magnesium metal with capacity of 94,500 tonnes/year[32,33].

2.5.2: Gossan Resources Ltd.

The Gossan Resources[34] Inwood Project is located in south-central Manitoba approximately 80 km north of Winnipeg. Gossan owns a dolomite deposit, which is estimated to have about 100 million tons of high-grade dolomite with less than 0.23 wt% impurities. In the fall of 2003, a 75 kilogram sample of dolomite was tested by Mintek and found to be suitable for a new silicothermic process[35]. In March 2004, Gossan ordered a series of feasibility studies by Hatch Associates Ltd.[36,37]. Currently, an initial economic assessment utilizing Mintek of South Africa's new atmospheric pressure silicothermic magnesium extraction process is underway. If technically and economically feasible, Gossan Resources intends to construct a 50,000 tonnes/year plant in Manitoba[38].

2.5.3: Leader Mining International Inc.

In May 2001, Leader Mining Inc.[39] entered in to an agreement to acquire 100 % ownership of the Cogburn Magnesium Project located approximately 100 km east of Vancouver, British Columbia. Sampling was followed by an economic and engineering study conducted by Hatch Associates Ltd. that confirmed economic viability for 131,000 tonnes/year magnesium production[6]. Leader also signed a technology transfer agreement with VAMI/STI to use its carnallite electrolysis process[5,40].

2.5.4: Troutline Investment Inc. (Cassiar Resources Inc.)

Troutline[41] completed the disposal of its abanded mine site in northern British Colombia containing the company's chrysotile and magnesium resources. This property constituted the only active business of the company. The company's interest in a construction of magnesium production plant based on residues of asbestos shifted to oil and gas investments[42].

2.5.5: Thetford Mines

The town of Thetford Mines, Quebec, continues work on proposal to process mining residue from asbestos mines into magnesium metal and other products[32].

2.6: Commonwealth of Independent States (CIS)

CIS's magnesium producers use carnallite based technology developed by Russian National Aluminum–Magnesium Institute, VAMI[43] and the State Titanium Research and Design Institute, STI[44]. These institutions have provided know-how and design engineering for construction of several plants such as the Zaporozhsky Titanium-Magnesium Plant (ZTMP) and Dneprovsky Titanium Sponge Plant. CIS production capacities have been variable in recent years due to their aged facilities, power shortages and financial instabilities.

2.6.1: Russia

Russia's magnesium production is concentrated in Avisma Titanium-Magnesium Works (Berezniki plant)[45] with 20,000 tonnes/year and Solikamsk Magnesium Works[46] with 24,000 tonnes/year production capacity, respectively. The country produced 45,000 tones of magnesium in 2003, which was a decrease from the 50,000 tones production record in 2002[47].

2.6.2: Kazakhstan

The Ust-kamenogorsk Plant is the only producer of magnesium in Kazakhstan and has reportedly increased its production in January-February 2004 by 15 % from 14,000 tonnes/year[48]. Kazakhstan produced 14,000 tons of magnesium in 2003, which was a decrease from 18,000 tones in 2002[47].

2.6.3: Ukraine

Different ventures and financial institutions such as Magnesium Elektron Ltd. have studied restarting of the Kalush Magnesium Plant in the Ukraine[49]. The plant, which once had 17,000 tonnes/year capacity was closed in 1998 when its production capacity was only 5,043 tonnes/year. The plant used to produce magnesium as a byproduct of potassium fertilizer production[50].

2.7: United States of America

Since February 2003, US Magnesium LLC[51] has returned to its full annual capacity of 43,000 tonnes/year after installing new technology at its production site in Rowley, Utah. US Magnesium has consolidated its production into two buildings and as result expects to produce the same quantity of metal with fewer electrolytic cells. The company confirmed that its Building One was fitted with 30 new 'M-Cells" that should yield 30,000 tonnes/year[52,53]. They also upgraded Building Four to produce another 13,000 tonnes/year of magnesium. U.S magnesium also assessed the feasibility of increasing its production to 80,000 tonnes/year by putting the new cells into other two closed buildings[54].

2.8: Israel

Dead Sea Magnesium Ltd.[55] uses the most advanced technological features of the Russian carnallite based technology[43,44] at its Sdom plant. DSM produces magnesium from the Dead Sea in conjunction with the Dead Sea Potash Works Ltd. DSM is owned by Israel Chemical Ltd. (65 %) and Volkswagen AG (35 %). This ownership guarantees DSM a metal market in the European community. Production capacity of the Sdom plant is 35,000 tonnes/year. The company produced 30,000 tonnes/year of magnesium in 2003, which was a decrease from its 2002 output of 34,000 tonnes/year[47].

2.9: Brazil

Rima Industrial S/A[56] is the only primary producer of magnesium in South America. Rima owns considerable dolomite reserves, which are used as a primary raw material in the production of magnesium and its alloys. Rima has 12000 tonnes/year production capacity but in 2003 produced only 6000 tones of magnesium[47]. In April 2003, the Brazilian Government began an investigation into the dumping of magnesium ingot imported from China into the Brazilian market. The government is expected to finalize its investigations within 1 year[6].

2.10: Australia

Australia has the most ambitious plans for the production of magnesium. At least five companies are actively pursuing magnesium projects. These companies have deeply suffered from the failure of the AMC project but still remain hopeful.

2.10.1: Australian Magnesium Corporation Ltd.

On March 2004, the Australian Federal and Queensland State governments decided to end their involvement with Australian Magnesium Corporation (AMC)[57] in the wake of its failed magnesium smelter[58]. As part of the agreement, AMC will reimburse A$46.4 M to the governments, the land that would have used as a plant site, and the physical and other assets that are not required to implement the company's new business plan[2]. AMC will continue the business of Queensland Magnesia Corp. (QMAG) magnesia and the development of its magnesite resources, its magnesium pilot plant, its assets and the intellectual property associated with the advanced magnesium technology. In April 2004, an A$200 M shareholder-called action was being planned over the collapse of Australian Magnesium Corporation's Stanwell Light Metals Project. The project collapsed in June 2003 after AMC ran out of money and was unable to find investors to accept the completion risk in the absence of a fixed price contract. The final cost to taxpayers of the failed project was A$240 M[59].

2.10.2: Magnesium International Ltd. (MIL)

Magnesium International Limited[60] (MIL), formerly Pima, is persuing the SAMAG project in Queensland, Australia. MIL will use the modified Dow process[60] for construction of its plant that will have 41,000 tonnes/year production capacity. Within two years, capacity will be increased to 84,000 tonnes/year. In February 2004, the company announced that they are evaluating the site of Stanwell Industrial Park, west of Rockhampton in central Queensland for construction of their plant. It was stated that electricity in southern Australia costs A$0.39/MWh compared to A$0.32/MWh in Queensland and further discounts might be obtainable since the location would be very close to the Stanwell power plant. MIL will source its magnesite ore from the extensive deposit around Yaamba, which is approximately 45 km north of Rockhampton[61].

Magnesium International Ltd. also extended its contract with ThyssenKrupp Metallurgie[62] to sell its total project output[63].

2.10.3: Latrobe Magnesium Ltd. (LMG)

Latrobe Magnesium Limited (formerly Rambora)[64] plans to produce magnesium from fly ash from the Hazelwood Power Plant in Victoria. Hazelwood uses brown coal and produces fly ash that is unusually has high magnesium content. LMG is in the process of undertaking a bankable feasibility study (BFS) in order to further progress the project and establish its economic viability as required by the banking community. The study will involve establishing an on-site pilot plant and securing the fly ash feed from the Hazelwood Power Plant. LMG plans to have full production underway by late 2010 with an estimated capital cost of A$857M. LMG originally intended to use dehydration technology developed by ALCAN[65,66]. However, in the current market conditions and to avoid funding an expensive pilot plant, LMG is considering using the proven VAMI/STI Russian technology[67]. In a recent report, LMG also reported plans to build its plant at Yallourn power station rather than at Hazelwood. The final decision will be made on the relative costs of transporting ash to from both sites[68,69].

2.10.4: Pacific Magnesium Corporation (Golden Triangle)

Pacific Magnesium Corporation[70] is persuing an electrolytic magnesium production project with a capacity of 80,000 tonnes/year of magnesium based on the Main Creek magnesite deposit in Tasmania and Woodsreef serpentinite tailings in New South Wales. The company has had hydrometallurgical test work performed by Lakefield Research Limited of Canada followed by the laboratory stage tests performed by Oretest Pty Ltd. Engineering Company[71]. The company's previous plans to use ALCAN[65,66] dehydration and electrolysis technology currently has also been shifted to the Russian VAMI/STI technology. Golden Triangle Resources also announced the development of a new electrolysis system, for which it has applied for a patent. The new electrolytic system, which was developed by the Joint Israeli-Russian Laboratory for Energy Research at Ben-Gurion University, will have the added advantage of significant energy savings for the magnesium production process[72].

2.10.5: Indcor Corporation

Indcor[73], formerly Crest Resources Magnesium NL, owns 100 % of Tasmania Magnesite NL which owns 100 % of the Lyons River and Arthur River magnesite tenements in north western Tasmania. Indcor completed extensive geological and metallurgical evaluations of the TasMag Project from 1998 to 2001. In 2001, Indcor planned to sell TasMag project in part or whole but since market and industry conditions were not favorable at that time, the sale was unsuccessful. In 2003, the company continued to review alternative process technologies to manufacture magnesium metal form magnesite[74].

2.10.6: New World Alloy Ltd.

New World Alloys Ltd.[75], formerly known as the Mt. Grace Resources, incorporated in 1998 following the exploration of substantial body of magnesite ore in the Northern Territory, Australia. New World worked with the "Heggie Group" and later with Mintek to evaluate the possibility of magnesium production that was followed by a feasibility study conducted on the company's site by Bateman/Multiplex Engineers[76]. The study proposed, as an initial plan, production of 12,500 tonnes/year magnesium, which could be scaled up in different stages to produce 50,000 tonnes/year. In the second half of 2002, the company decided to look beyond the existing boundaries of the company's assets and to launch another feasibility study, based on a '*Malaysian-model*' where a high quality resource was known.

The *Malaysian-model* business plan was to purchase and relocate the 90,000 tonnes/year decommissioned Addy Magnesium Plant owned by ALCOA[77] from Washington State to Perak State, Malaysia. To this end in February 2003, a consortium of Malaysian investors was established to partner with New World Alloy (NWA). The complex financial arrangements that were required to fund the US$150M plant required ALCOA to extend the sole option to purchase the plant. Since this undertaking was not forthcoming the business plan failed to initiate[78].

2.11: Congo Republic

2.11.1: Magnesium Alloy Corporation

Magnesium Alloy Corporation[79] "MagAlloy", is developing a 60,000 mpta smelter following the completion of a positive feasibility study performed by Salzgitter Anlagenbau GmbH (Salzgitter) of Germany. MagAlloy's Kouilou magnesium project is located in Pointe-Noire, Republic of Congo (Congo-Brazzaville). The project aims to utilize low cost hydroelectric and natural gas energy together with KBB[80] solution mining and VAMI/STI carnallite based technology[43,44]. The plant design engineering and construction consortium will be led by Ferrostaal AG[81]. MagAlloy also has formed a wholly owned subsidiary, MagEnergy, to construct the Inga hydroelectric plant[82] and transmission lines with cooperation of Eskom Enterprise Ltd[83].

2.12: Netherlands

2.12.1: Antheus Magnesium B.V.

Antheus Magnesium B.V.[84,85,86] is in the financing stage to build a magnesium plant in the Delfzijl Industrial Park, Netherlands to produce 50,000 tonnes/year of magnesium from magnesium chloride. Start-up of the plant is not expected until 2006 and the estimated capital cost of the project is US$ 255M[87,88].

2.13: Recent Developments

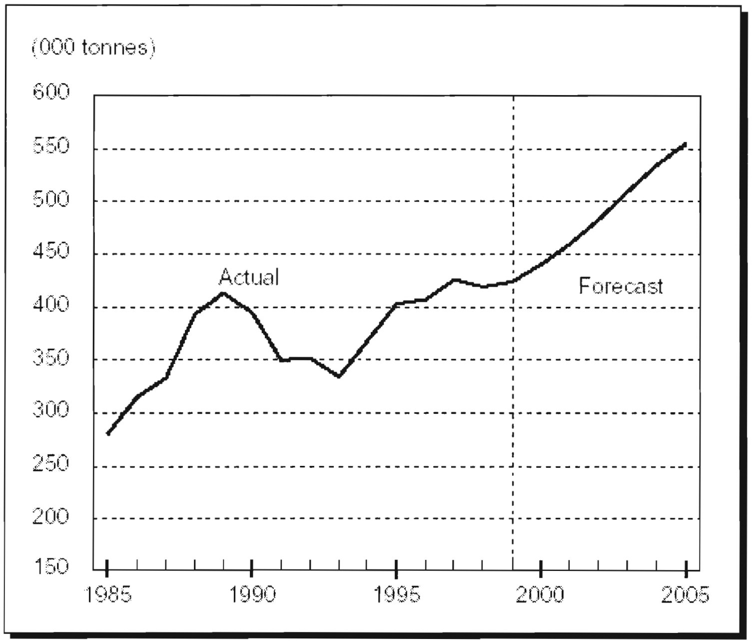
On February 17, 2004, U.S. Magnesium LLC filed a petition with U.S. International Trade Commission (ITC) claiming that imports of magnesium alloy from Russia were harming the U.S. industry. After US Trade preliminary approval to impose anti-dumping duties on magnesium metal imported from Russia and China, the U.S. International Trade concluded that there was a reasonable indication that lower priced imports from the two countries were harming U.S. producers. After a hearing on March 19, 2004, the U.S. Department of Commerce, International Trade Administration (ITA) began its investigation into the claim. In 1995, the ITC had determined that the import of pure magnesium from China was injuring the U.S. magnesium industry and set a duty rate of 108.26 % ad valorem for pure magnesium, but no duty was established for alloy magnesium. After a new investigation begun in 2000, the ITC established a duty of 305.56 % ad valorem as the China wide rate for granular magnesium, which was not covered by the 1995 determination. In both instances, magnesium from Russia had been investigated along with magnesium from China, but it was determined that import of pure, alloy, and granular magnesium from Russia did not injure the U.S. industry, so no duty rate was established. On April 12, 2004, the ITC determined that there was a reasonable indication that U.S. industry was materially injured by imports of pure magnesium from Russia and alloy magnesium form China and Russia that were sold at less than their fair values. As a result of the ITC's affirmative determination, the ITA will continue to conduct the anti-dumping investigation with its preliminary antidumping determination due by August 5, 2004[36]. In 2003, the USA imported 23,700 tones magnesium from Canada (43 %), China (18 %), Russia (17 %) and Israel (11 %)[1,47].

The South African minerals-technology organization, Mintek[35] is developing a thermal process with DC-arc technology to produce magnesium continuously and will seek to commercialize it with its with its partners by the middle of 2004. The technology involves continuous feeding of calcined dolomite and ferrosilicon into an electric furnace to produce magnesium vapor, which enters a unit where it condenses into liquid metal and slag, at a slag to metal ratio of six to one by mass. The silicothermic reaction is carried out at atmospheric pressure instead of under a vacuum as in the conventional Pidgeon process. Mintek's process has no problem with vacuum leakage and the consequent reoxdiation of magnesium. The company has stated that the slag could find applications in the cement making industry. The need for hot feeding of the furnace with calcined dolomite at temperature above 600 °C was also established. The process was designed to minimize the labor required to produce magnesium as compared to a thermal batch process used in China. This would allow producers in countries where labor costs are higher than those in China to compete economically[89].

The Federal Government of Australia created the Light Metals CSIRO-Flagship[90,91]. This light metals initiative aims to double the economic value of Australian light metal production to A$104B by 2010, cut by one third the energy needed to make light metals, develop new technologies to create a new titanium metal industry and cut the life–cycle environmental impact of light metal products by 50 %.

2.14: Magnesium Applications

The magnesium industry today is at a similar stage of development of applications as the aluminum industry was in the 1960's. Growth in demand for magnesium will increase as the scale of magnesium metal production plants increases, thereby causing a reduction in production costs. Figure 1 shows world magnesium consumption between 1985 and 2005. Magnesium consumption is expected to increase to over 600,000 tonnes/y by 2005.



Source: Natural Resources Canada.

Figure 1: World Magnesium Consumption 1985-2005.

Currently, the average North American–produced family vehicle contains about 4.5 kg of magnesium castings. This quantity has been increasing each year and has doubled in the last 10 years[47]. With the number of applications being developed by automotive manufacturers, this annual growth is expected to continue at a high rate. It has also been predicted that the automotive use of magnesium will increase to more than 15 kg per vehicle by 2015[47,92]. If this occurs, it will result in an annual demand of 1 million tones of primary magnesium metal per year. The growth of magnesium usage in automotive applications will occur through an increase of the magnesium share in other materials used in existing applications, development of new component applications, development of new magnesium alloys and improvements in die-casting.

The motivations for automotive manufacturers to consider using magnesium to reduce vehicle weight are to improve fuel economy, reduce pollution, improve handling and driver feel characteristics, replace the number of multi-piece steel or aluminum components with fewer magnesium alloy die-cast parts and a desire to avoid the use of plastics, which are difficult to recycle. Although weight reduction is the main reason that automakers are looking at magnesium, the high productivity of magnesium die-casting operations and the long tool life associated with magnesium parts production also favor the metal. If metal prices stay low and stable, magnesium might soon find itself being used for major structural and power train components such as engine sub-frames, cylinder blocks, intake manifolds, transmission cases and door frames.

2.15: Financial Aspects

There are strong indications that the recent slowdown in Chinese economic growth due to power availability, shipping constraints, and raw materials prices will end soon and Western producers will have to face a tough fight to protect their production[93]. It was estimated that costs of produced magnesium from new production must be in the range of 1.326 to 1.432 US$/kg to compete with China on a cost basis. This means bringing magnesium to market at about 2.645 to 2.865 US$/kg for the full cost of production. Current U.S. spot magnesium prices are in arrange of 3.417 to 3.638 US$/kg[94].

2.16: Conclusions

Unlike other mature metals for which demand is determined mainly by economic capability of important end-users, future demand for magnesium alloys will be determined by actions taken by magnesium producers and die casters. Governments and the main metal producers should cooperate to develop reliable technologies capable of handling different magnesium resources. Projects need to be based on proven technologies, which in turn provide the possibility of fix-price construction contracts thereby lowering the risks of investment. Die casters also should participate in R&D activities to develop new alloys with better high temperature mechanical and physical properties and at the same time improve their casting capabilities. New alloys and more efficient casting techniques will result in finding new applications for magnesium alloys and boosting magnesium position as a structural metal.

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Chapter 3: Technological Review of Anhydrous Magnesium Chloride Preparation

3.1: Abstract

All electrolytic magnesium production processes electrolyze $MgCl_2$ in a bath of molten salt, but the processes substantially differ from one another in their preparation of the magnesium chloride feed for the electrolysis. The common challenge is that the magnesium chloride loaded, fused-salt electrolyte must be virtually free of oxygen and/or oxygen containing compounds that result from the significant difficulty in producing anhydrous magnesium chloride due to its very hydroscopic nature. The commercial failures of several recent electrolytic magnesium production ventures have resulted in the environmentally less-favorable, thermal reduction route to become considered the more reliable method for new magnesium production. The purpose of this article is to summarize the main designs of anhydrous magnesium chloride production processes, namely, the dehydration of magnesium chloride hydrates or double salts in a controlled HCl-H_2O atmosphere, the chlorination of magnesium oxides, the dehydration of magnesium chloride and ammonia double salts, the application of ethylene glycol and the application of analytical methods for production of anhydrous magnesium chloride. The benefits of scale available from the electrolytic processes as compared to the current thermal routes will promote on-going exploration and development of new feed preparation process in response to the increasing demand for magnesium. It is also clear that this field would benefit from fundamental studies and validation of some the basic principals.

3.2: Introduction

There are two generic processes for the commercial production of magnesium. One involves thermal reduction of magnesium oxide compounds under vacuum and the other involves electrolytic reduction of magnesium chloride dissolved in a molten or 'fused-salt'. The growing application of magnesium has resulted in an increased demand for this metal[1]. Several unsuccessful attempts at developing new electrolytic magnesium production have resulted in the environmentally less-favorable thermal reduction route becoming considered the more reliable method for production of magnesium[1]. At the present time, the thermal reduction route contributes more than 60 % of world's magnesium production. However the electrolytic route is more amenable to scale-up and reduction of operating costs as well as having a less negative impact on the environment per kilogram of produced magnesium[2]. As a result, the latter still needs to be considered for new magnesium production capacity in the future.

The electrolytic route was first proposed by Bunsen in 1865 and first tried in Germany in the late 1800's. It was commercialized by Dow Chemical Company in the USA in 1916 and has been extensively developed since that time. Germany was also very active in the development of the electrolytic process[3,4]. A number of other ventures have also developed commercial variations of the electrolytic route, but each commonly purifies an aqueous solution containing magnesium chloride to produce a nominally anhydrous, magnesium chloride feed for the electrolytic operation.

Examination of the thermodynamics of the precipitation of magnesium chloride from aqueous solution reveals that the first solid to precipitate under uncontrolled conditions is magnesium chloride hexahydrate ($MgCl_2.6H_2O$)[5], but unless special and expensive precautions are undertaken, the product of dehydrating $MgCl_2.6H_2O$ contains significant quantities of oxygen-containing compounds that will enter and contaminate the fused salt electrolyte[6]. The early commercial response to this issue was to operate cells tolerant of the oxide contamination but with higher costs. Later, it was considered better business to produce and use oxide free material, which it will be shown below must be in the form of anhydrous magnesium chloride, as the cell feed at higher cost but which allows more energy efficient electrolysis and the production of not only magnesium metal but also marketable chlorine gas. There were two approaches to the problem, chemical treatment to avoid or reverse the problems arising from hydrolysis and/or physical treatment. Chemical treatment has been the industry's preferred methodology, but physical treatment has it merits due to its simplicity even if it is not practiced, and is briefly described below.

The density of magnesium oxide is higher than that of molten magnesium chloride and most of the magnesium chloride bearing fused-salts. As a result, magnesium oxide particles separate from the molten salts by forming sludge at the bottom of the melt container. This behavior was used as means for purifying industrial electrolytes of magnesium oxide. Such a technique requires a considerably long holding time at a temperature well above melting point of the molten salts and results in the formation of a solid sludge at the bottom of the settler, which grows gradually and needs to be removed periodically.

Matthey et al.[7] proposed a method in 1931 for the decanting the molten magnesium chloride and oxides from each other after two hours of holding at 780 °C. Consolidated Mining and Smelting Company of Canada[8] developed another process in 1946 for the sedimentation refining of magnesium oxide from molten magnesium chloride by adding cell mud. Lloyd[9] from Titanium Metals Corporation of America described a process in 1969 for treating hydrated magnesium chloride comprised of drying the magnesium chloride, melting the dried magnesium chloride to produce a mixture of a liquid and slurry, superheating the mixture at a temperature of at least 912 °C to decompose any magnesium hydroxychloride to MgO and decanting the liquid from the slurry.

Another physical separation technique that has been developed exploits the solubility of magnesium chloride in low boiling point alcohols such as methanol and ethanol vs. the insolubility of magnesium oxides. Dissolution of a mixture of magnesium chloride and magnesium oxides in these alcohols followed by a filtration process results in the physical separation of magnesium chloride in the form of a raffinate from the magnesium oxide in the form of a residue. Magnesium chloride can be recovered by heating the raffinate.

Chimiques Et Electrometallurgiques Alais[10] described a process in 1925 whereby carnallite or magnesium chloride can be separated form their impurities such as NaCl or MgO by the means of alcohol dissolution followed by a distillation separation at 200 °C. Levy[11] developed a process in 1953 for the separation of magnesium chloride from a solid mixture of magnesium chloride and other chlorides with the aide of acetone.

The story of chemical treatment is far more complex. The oxygen-containing compounds that can be found in the products of $MgCl_2.6H_2O$ dehydration are either in the form of crystalline MgO or as 'hydroxychlorides'. The amount and composition of oxide species formed during the dewatering of the magnesium chloride aqueous solution is believed to be controlled by a number of parameters, such as the kinetics of dehydration and the temperature and HCl content of the dehydration atmosphere[12].

After a brief presentation of the thermodynamics of dehydration of $MgCl_2$, it is the purpose of this article to review the various methods to produce anhydrous magnesium chloride or at least a feed for the electrolysis cells free from magnesium oxide or hydroxychloride compounds and thus to summarize the application of the various few novel ideas in this field.

3.3: Equilibrium Dehydration of Magnesium Chloride Hydrates

The $MgCl_2$-H_2O phase diagram shows that at room temperature the fully hydrated form of magnesium chloride is the hexahydrate, $MgCl_2.6H_2O$. Upon heating, this salt undergoes stepwise dehydration first forming magnesium chloride tetrahydrate which further dehydrates to magnesium chloride dihydrate. The dehydration of magnesium chloride hexahydrate to dihydrate presents no particular problem under ambient atmosphere, but dehydration to $MgCl_2$ by heating the dihydrate requires special precautions and without sufficient HCl partial pressure in the atmosphere leads to the formation of MgOHCl[5], Reactions 1 and 2.

$$MgCl_2.2H_2O_{(s)} = MgOHCl_{(s)} + HCl_{(g)} + H_2O_{(g)} \qquad (1)$$

$$MgCl_2.H_2O_{(s)} = MgOHCl_{(s)} + HCl_{(g)} \qquad (2)$$

$MgOHCl_{(s)}$ decomposes at 555 °C to MgO and HCl according to, Reaction 3[5].

$$MgOHCl_{(s)} = MgO_{(s)} + HCl_{(g)} \qquad (3)$$

Equilibrium dehydration in atmospheres containing sufficient $HCl_{(g)}$ suppresses hydrolysis Reactions 1 and 2 and results in the formation of anhydrous magnesium chloride according to Reactions 4 and 5.

$$MgCl_2.2H_2O_{(s)} = MgCl_2.H_2O_{(s)} + H_2O_{(g)} \qquad (4)$$

$$MgCl_2.H_2O_{(s)} = MgCl_{2(s)} + H_2O_{(g)} \qquad (5)$$

This approach was used as the basis of many industrial dehydration processes but only with limited success due to kinetics and mass transfer factors that play a role in determining the rates and extents of dehydration in any particular operation. To this end, Barstow[12] from DOW Chemical Company stated in 1931 that the dehydration atmosphere couldn't influence the formation of oxides during the dehydration of magnesium chloride hexahydrate. The present authors have recently confirmed such behavior[13]. It should also be noted that the industry has been hampered until recently by the lack of a reliable analysis technique to identify and quantify the non-equilibrium products with the result that process optimization was always backward looking, that is, they had to process the feed through the electrolysis cells to determine the efficacy of dehydration, and was thus inherently uncertain[14,5].

Another aspect of the thermodynamics that has been exploited commercially is the beneficial effect of lowering the activity of $MgCl_2$ and hence the lowering of the tendency for its hydrolysis by either adding the magnesium chloride into a molten salt solution that exhibits negative deviation from ideality for the magnesium chloride or by reacting it with a compound such as potassium chloride or ammonium chloride to stabilize it.

3.4: Hydrochlorination and Carbochlorination Processes

Hydrochlorination and carbochlorination are chemical processes that can serve two purposes. They can involve the non-aqueous reaction of magnesium oxide or magnesium hydroxychloride compounds with chlorine in the presence of hydrogen, carbon or carbon containing species. The hydrogen, carbon or carbon containing species provide a stable oxygen-containing reaction product that offsets the equilibrium in favor of the chlorination reaction. Alternatively they involve the suppression of the hydrolysis of magnesium chloride, i.e., the reaction of $MgCl_2$ with moisture to form MgO or magnesium hydroxychlorides and HCl, if any depending on the form of the oxide, during its production.

In subsections below, the suppression of hydrolysis, the conversion of inadvertently formed magnesium oxide and hydroxychloride, i.e., the back-chlorination of the hydrolysis products and/or the beneficial effect of lowering the activity of $MgCl_2$ are the focuses of the described technologies

3.4.1: Suppression of Hydrolysis Reactions

In 1919, Ashcroft[15] described a process for production of discrete particles of high-density anhydrous magnesium chloride. In his process, concentrated brine was spray dried at 150 °C to form a partially dehydrated magnesium chloride that was followed by final dehydration in a stream of H_2O-HCl at 650 °C to produce dense magnesium chloride particles.

Cottringer et al.[16] proposed two designs for the dehydration of hydrates in shelf-type or rotary dryers in 1923. They stated that the presence of dry hot HCl gas was necessary to convert any hydrolysis products that possibly formed but that the use of HCl in the primary dehydration atmosphere reduces its efficiency. Thus they intended to have a temperature gradient in their reactors into which bischofite would be fed at the entrance and would loose all of its water in a counter current stream of HCl. Collings et al.[17] from Dow Chemical Company described a similar process in 1924 using an externally heated rotary dryer. However it became well known that dehydration of magnesium chloride hexahydrate to magnesium chloride dihydrate could be done in a stream of hot air with minimum risk of oxide formation with the result that a major development in this field related to the adoption of a two-stage dehydration process whereby dehydrated magnesium chloride could be produced in a simple fluidized bed or spray drier in a first stage and final dehydration would be performed in second reactor with a high efficiency of HCl utilization.

Dow Chemical Company in a 1926 patent[18] described a process whereby magnesium chloride hexahydrate was dried in air to produce magnesium chloride dihydrate and then anhydrous magnesium chloride was produced in a rotating-shelf-dryer in a counter-current stream of HCl at 500 °C.

Griessbach et al.[19] from IG Farben proposed a process in 1928 whereby the final dehydration of a feed composed of partially dehydrated magnesium chlorides occurred at 300 °C in a stream of HCl/N_2 with a composition ranging from 10 to 20 wt% HCl. They reported that the final product contained between 1.3 to 5.3 wt% oxide and 1.4 to 4.9 wt% water.

Heath[20] from DOW Chemical Company proposed a process in 1933 whereby the monohydrate was dehydrated in a hot stream of HCl to produce $MgCl_2$ in a powder form.

Lyons[21] from National Lead Company developed a process in 1967 whereby magnesium chloride brine was dehydrated to dihydrate in a spray dryer at 196 to 274 °C. Final dehydration was performed in a fluidized bed furnace in the presence of a stream enriched with the HCl at 260 to 343 °C for the production of very fine magnesium chloride powder.

Larson et al.[22] from Dow Chemical Company described a process in 1970 whereby small particles of magnesium chloride dihydrate and a mixture of air and HCl were blown in to a Dycoor reactor at 450 °C to produce anhydrous magnesium chloride. They suggested that the ratio of HCl/H_2O in the reactor had to be at least 4/1.

Norsk Hydro patented prilling processes for the production of magnesium chloride[23,24,25] in 1973 and 2001. They claimed that to prevent extensive metal loss and the materials handling problem of fine dust, the partially dehydrated magnesium chloride feed had to have the tetrahydrate composition. They also stated that depending on the type of dehydration reactor to be used, for example a fluidized bed or a rotary kiln, molten tetrahydrate would be prilled in a counter current fluidized bed dryer or a rotating disc pelletizer, Figure 2 and Figure 3. In a second stage of dehydration, dihydrate was produced followed by two or three stage dehydration in an HCl enriched atmosphere to produce anhydrous magnesium chloride. These secondary dryers were in series and were constructed one above the other; HCl gas being flowed upward through the fluidized beds counter-currently. The temperature of the three fluidized drying beds were 330, 250 and 180 °C, respectively.

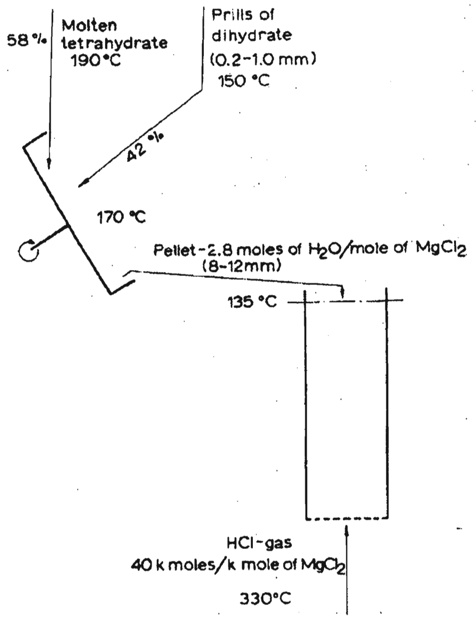

Figure 2: Norsk Hydro Rotating Disc Prilling Process.

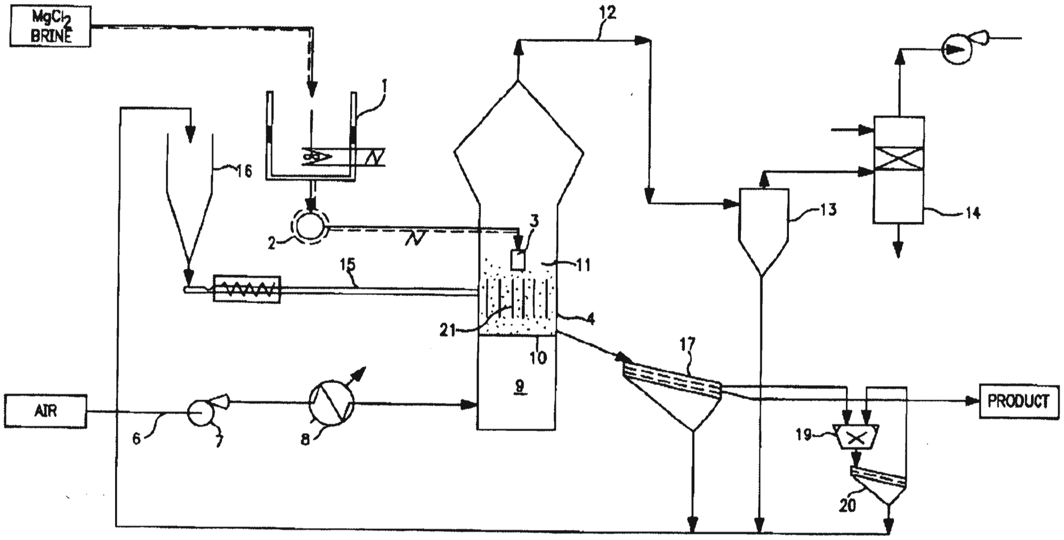

Figure 3: Norsk Hydro Fluidized Bed Prilling Flow Diagram.

1: Feed tank, 2: Pump, 3: Spray nozzles, 4: Fluidized zone, 7: Centrifugal fan 11: Fluidized bed, 13: Cyclones, 14: Wet scrubber, 16: Silo, 20: Screen

Norsk Hydro both at Pasgrunn, Norway and in Becancour, Quebec, Canada is the only company that has practiced this technology, which dries $MgCl_2$ all the way to anhydrous without the use of some type of chlorinator to back-react any oxide inadvertently formed. Norsk maintains a drying atmosphere high in HCl to drive off all the water and avoid the hydrolysis reactions. The cell feed produced by this process is a solid granular material that can be conveyed using conventional bulk handling methods. The systems must be well sealed in order to avoid moisture pickup. Norsk has had to overcome significant technical challenges, for example, large amounts of HCl containing process gas needed to be handled and recirculated and the process has high-energy consumption. However, the Norsk system allows for considerable automation of the subsequent cell process and for the finer control of the cell bath chemistry.

3.4.2: Bone Dry Dehydration of Hydrates and Back Chlorination of Oxides

The production of feed by adjusting dehydration atmosphere at a commercial scale poses significant technical difficulties. Thus complete dehydration of hydrates without manipulating the dehydration atmosphere and then back chlorination of oxides that form has been pursued commercially. This approach minimizes process gas handling but the rate of back chlorination varies considerably with the composition of oxides and chlorination conditions.

Hulin[26] applied this concept in 1918 and described a process for the preparation of anhydrous magnesium chloride in the presence of HCl gas. Barstow[12] described a cyclic process for back chlorination of MgOHCl with HCl at 280 °C to monohydrate, which could be further dehydrated to magnesium chloride with lower oxide content.

Shell International[27,28] developed a process for the dehydration of magnesium chloride hexahydrate to magnesium chloride with less than 0.5 mole H_2O per mole magnesium in a spray drier. The dehydrated products were then pelletized and fed to a shelf-type reactor in the presence of the HCl gas at 450 °C to produce anhydrous magnesium chloride.

Erneta[29,30,31,32] from NL Industry described a process whereby hydrous magnesium chloride was spray dried at elevated temperature for a period of time sufficient to partially hydrolyze the magnesium chloride and reduce the chemically bonded water to 3 wt%, then followed by chlorination with HCl at 260 to 427 °C to reduce the feed oxide content to 0.6 wt% MgO.

3.4.3: Hydrochlorination of Magnesium Oxides

Another approach to the production of magnesium chloride is the chlorination of natural sources of magnesium oxide with HCl. Barstow[33,34] from Dow Chemical Company found that a mixture of magnesium chloride and MgO that can be represented as $3MgO.MgCl_2.10H_2O$ can be prepared by mixing magnesium chloride brine and magnesium oxide. The cement that was produced, thought to be magnesium chloride hydroxychloride, was crushed, dehydrated and back chlorinated to $MgCl_2$ at about 300 °C, Reaction 6.

$$MgOHCl_{(s)} + HCl_{(g)} \rightarrow MgCl_{2(s)} + H_2O_{(g)} \qquad (6)$$

Fukuzawa et al.[35] developed a process in the 1970's for the production of anhydrous magnesium chloride consisting of the precipitation of magnesium carbonate with 3 molecules of the water that was dehydrated in a rotary dryer to anhydrous magnesium carbonate that was subsequently chlorinated at a high rate at 350 to 550 °C according to Reactions 7 and 8.

$$MgCO_{3(s)} + HCl_{(g)} \rightarrow MgOHCl_{(s)} + CO_{2(g)} \qquad (7)$$

$$MgOHCl_{(s)} + HCl_{(g)} \rightarrow MgCl_{2(s)} + H_2O_{(g)} \qquad (8)$$

3.4.4: Dehydration of Hydrates in the Presence of Fused-Salts

The activity of magnesium chloride exhibits considerable negative deviation from ideality in some fused-salt mixtures. As a result, the feeding of magnesium chloride hydrates to fused-salt baths allows dehydration to be performed with lower risk of hydrolysis. This concept was used in the development of some industrial dehydration processes as described below.

IG Farben[36] developed a process in 1929 whereby magnesium chloride dihydrate was produced from air dehydration of magnesium chloride hexahydrate. The magnesium chloride dihydrate was then fed into a molten salt bath consisting of $MgCl_2$-NaCl-KCl at 700 °C. It was reported that a very small amount of the magnesium salt decomposed to magnesium oxide. Lacell[37] suggested a process in 1931 whereby magnesium chloride hexahydrate was fed to a large bath of molten magnesium chloride at 500 °C. She also reported small amount of magnesium oxide formation.

In 1934 Moschel[38] described the addition of magnesium chloride dihydrate directly to the electrolysis cells, which contained a molten electrolyte composed of KCl-NaCl-$MgCl_2$ at 700 °C. The feeding rate of magnesium chloride dihydrate was selected such that the $MgCl_2$ content of the mixture did not exceed the proportion prevailing in natural carnallite. Mathieson Alkali Works[39] also described a process in 1941 for the final dehydration of magnesium chloride hydrates by feeding them to a molten salt mixture of different alkali and alkaline chlorides.

Dow Chemical Company developed this technology, which allows the electrolytic cells to be fed with partially hydrated $MgCl_2$[5]. Such feed was a granular solid and was easily conveyed to the electrolytic cells. The main disadvantage of this technology was that it used the electrolytic cell to perform final drying of the feed and to some extent chlorination of some of the oxides that inadvertently formed. The prevalence of oxides in the cells lowered current efficiency and resulted in high electrode graphite consumption.

3.4.5: Hydrochlorination of Molten Salts

A refinement of the process above including the additional step of hydrochlorinating the oxides that formed in the bath with HCl gas has also been used for feed production. HCl reacts with the magnesium oxides and back-chlorinates them to magnesium chloride. The rate of the chlorination of the oxides varies greatly with the composition of oxides and the chlorination conditions. IG Farben[40] described such a process in 1928.

Bauer et al.[41] proposed a process in 1961 whereby a potash industry effluent enriched with magnesium chloride, which had a small amount of other alkaline chlorides similar to carnallite composition, was air dehydrated. The dehydration product was then melted in a cyclone reactor designed to separate the magnesium chloride and a sludge that was subsequently chlorinated to magnesium chloride.

Esoo Research and Engineering[42] developed a process in 1965 whereby molten magnesium chloride tetrahydrate was fed into a fluidized bed dryer at 326 °C with high HCl/H_2O ratio in the dehydration atmosphere. The impure magnesium chloride was fed into a molten salt bath where oxides were back chlorinated by the injection of HCl at 715 °C.

Shaw[43] from Esoo Research and Engineering described another process in 1968 whereby magnesium chloride hexahydrate was dehydrated in four stages resulting in the production of magnesium chloride with 4.6 to 4.8 molecules of water at 177 to 188 °C followed by the further dehydration in a fluidized bed dryer at 580 °C to produce magnesium chloride dihydrate. Magnesium chloride monohydrate was then produced in a third stage under an inert gas atmosphere and was later fed into a molten salt bath for final chlorination of any remaining oxide or back-reacted with chlorine at 788 °C.

Wheeler[44] proposed a process in 1978 whereby partially dehydrated magnesium chloride hydrate was fed into a molten salt bath at 600 to 800 °C wherein the oxides were chlorinated by the injection chlorine gas.

Peacey et al.[45] from Noranda Inc. developed a process in 1996 for the production a magnesium chloride containing melt or electrolyte containing less than 0.2 wt% MgO directly from hydrated magnesium chloride feeds. The process comprised the steps of: dehydration of concentrated magnesium chloride brine to magnesium chloride dihydrate, feeding this into a furnace containing a melt of molten electrolyte at 550 to 650 °C, injecting anhydrous hydrogen chloride gas into the melt in a rate above the stoichiometric requirement of 2 moles of HCl per mole of magnesium chloride in the hydrated magnesium chloride feed and agitating the melt to keep any magnesium oxide in suspension in the melt. This process was used for extraction of magnesium from serpentine ore ($3MgO.2SiO_2.2H_2O$) and was the basis of the Magnola Metallurgie Inc. plant in southern Quebec.

3.4.6: Carbochlorination of Magnesium Oxides

In carbochlorination processes, MgO or magnesium carbonates are reacted with carbon and chlorine to form $MgCl_2$. The overall process reaction is as follows:

$$2MgO_{(s)} + 2Cl_{2(g)} + C_{(s)} \rightarrow 2MgCl_{2(s)} + CO_{2(g)} \qquad (9)$$

Carbochlorination was usually performed in shaft type reactors filled with a mixture of magnesia or magnesite and carbonaceous materials. Chlorine was fed through tuyeres, Figure 4. Since the carbochlorination reaction is highly exothermic, electrodes were used mainly for initial heating. Carbochlorination was practiced in two ranges of temperature. At temperatures below the fusion temperature of magnesium chloride, it was found that diffusion of chlorine through a solid layer of magnesium chloride produced on the surface of unreacted oxides greatly limited the carbochlorination rate. On the other hand, at temperatures higher than the melting point of magnesium chloride the kinetics was fast but nonetheless, significantly influenced by the sticky, molten magnesium chloride that formed during the chlorination.

This technology was used by Norsk Hydro in Norway[46] (1921) and later by IG Farben in Germany[47,48,49](1926 to 1930). Figure 4 shows a schematic of their reactor. One of the biggest drawbacks of this technology was the generation of unwanted chlorinated compounds in the chlorination reactor due to the reaction of C and Cl_2 and the associated difficulties in disposing of these compounds. An additional difficulty was that the $MgCl_2$ had to be batch fed to the subsequent electrolysis cells with the result that electrolysis cell automation was difficult.

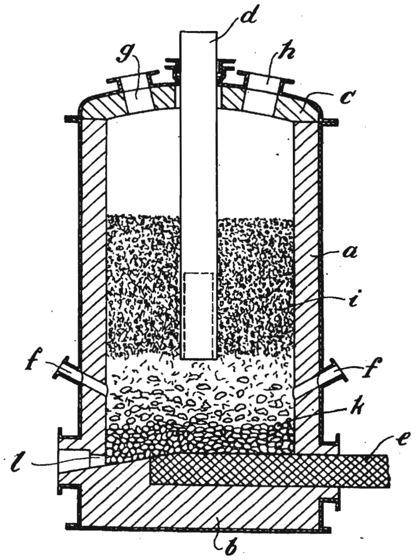

Figure 4: IG Farben Shaft Type Reactor.

Magnesium chloride brine was added to the MgO feed to produce porosity upon evaporation of water and thereby led to enhanced reaction kinetics. A: Refractory Lining F: Tuyere I: Charge

In another series of patents issuing from 1930 to 1937, IG Farben [50,51,52,53] claimed that for low temperature operations, magnesium oxide is not completely reacted to form magnesium chloride and the best possible chlorination rate only can only be achieved only if the charge material was the size of a nut, mixed with carbonaceous material and operated at 700 to 900 °C.

Magnesium Elektron Ltd.[54] in 1939 and Ebert et al.[55] in 1962 described a process for the production of the anhydrous magnesium chloride whereby lower hydrates of magnesium chloride were first produced in an air spray drier at 200 to 220 °C and then molten magnesium chloride was produced by the chlorination of the material in a shaft furnace with carbon at 800 to 900 °C. Magnesium Elektron Ltd.[56,57,58] developed another process in 1944 to 1946 for production of mechanically strong feed for use in a shaft-type carbochlorination furnace. The feed was made from caustic magnesia, magnesium chloride hydrates, brine and coal and produced a self-setting pellet. The Honorary Advisory Council for Scientific and Industrial Research of Canada[59,60] and Consolidated Mining and Smelting Company of Canada[61,62] described similar processes during the periods from 1940 to 1947 for the production of magnesium chloride by carbochlorination of the magnesia with coke or coal in a shaft furnace by injecting chlorine through tuyeres into the furnace at 1000 °C.

In 1981, Shackleton et al.[63,64] proposed a process of carbochlorination of solid pieces of impure magnesium carbonate in a packed bed reactor using gaseous chlorine in the presence of carbon monoxide at a temperature above the melting point of magnesium chloride and below 1200 °C. Carbon dioxide was withdrawn from the top of the packed bed and molten anhydrous magnesium chloride was withdrawn from the bottom.

Several Russian patents[65,66,67] in 1942, 1980 and 2001 respectively, described carbochlorination of carnallite. These processes comprised dehydration of carnallite by fuel combustion at 205 to 230 °C to produce a moisture content of 3 to 8 wt% followed by the final dehydration/chlorination of fused carnallite in a cyclone type furnace at 700 to 800 °C.

Peacey[68,69] developed a process in 1991 and 1999 for the preparation of anhydrous magnesium chloride comprised of feeding spray dried magnesium chloride or magnesia powder into a furnace containing a molten magnesium chloride melt at a temperature of about 750 to 850 °C. Figure 5 shows the configuration of the equipment used to develop his process. The loaded melt was reacted with a carbonaceous reductant and chlorine. The gases were introduced into the melt bath using gas disperser consisting of a rotating impeller having a hollow shaft for supplying gaseous carbochlorination agent. Gas bubbles having diameters smaller than 5 mm and having gas hold up as high as 30 v/v% of the original melt volume were used. Such operating conditions also ensured that the fine particles present in the melt were evenly suspended.

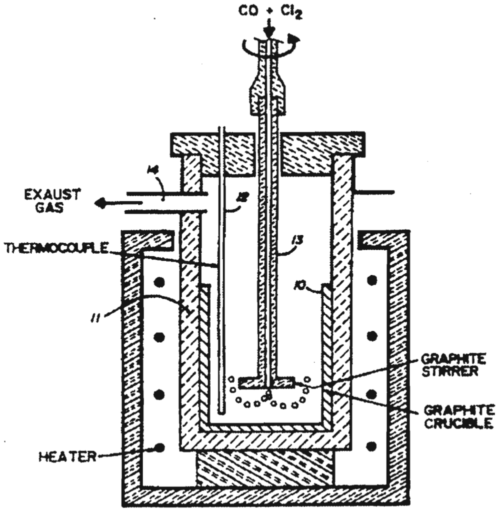

Figure 5: Peacey's Reactor.

Magcorp in Rowley, Utah practiced another variation of carbochlorination to produce anhydrous $MgCl_2$ after extracting the $MgCl_2$ from the Great Salt Lake[5] whereby they dried the $MgCl_2$ to a mixture of MgOHCl and $MgCl_2.H_2O$ and then fed this mixture into a molten salt bath where it was chlorinated with Cl_2 that came from the magnesium electrolysis cells. They also added coke to this reactor. The product of the reactor was further refined in a second reactor before it was fed to the electrolytic cells. It was necessary to batch feed the cells using a crucible to transport the feed.

3.4.7: Carnallite Process

Magnesium chloride and potassium chloride form a hydrated double salt called carnallite, $KCl.MgCl_2.6H_2O$. The dehydration of carnallite proceeds according to Reactions 10 and 11.

$$KCl.MgCl_2.6H_2O_{(s)} = KCl.MgCl_2.2H_2O_{(g)} + 4H_2O_{(g)} \quad (10)$$

$$KCl.MgCl_2.2H_2O_{(s)} = KCl.MgCl_{2(s)} + 2H_2O_{(g)} \quad (11)$$

The technology for dehydration of carnallite is similar to that used for dehydrating bischofite, but because carnallite can be dehydrated more easily due to lowering of the activity of the $MgCl_2$ by the KCl and the accompanying hydrolysis is less extensive than in the case of bischofite[5,6] and the technology demands are less stringent.

The Russian National Aluminium-Magnesium Institute, VAMI[70], and the State Titanium Research and Design Institute, STI[71], have jointly developed an electrolytic route for magnesium production based on use of natural carnallite as the raw material. Their process consists of the following stages: synthesis of carnallite from aqueous solution of magnesium, potassium and sodium chlorides or by recrystallization of natural carnallite, dehydration of the carnallite and finally electrolysis of the dehydrated product to produce magnesium and chlorine.

To produce synthetic carnallite, the process feed should have following composition, $MgCl_2$ (30 - 34 wt%), KCl (21 - 25 wt%), NaCl (3.5 - 9 wt%), $CaCl_2$ (~ 2 wt%) and H_2O (balance). Dehydration of synthetic carnallite is carried out in fluidized bed furnaces with the use of hot gases produced by fuel combustion. Dehydrated carnallite contains less than 0.3 wt% oxide and is melted and treated in a chlorinator at 800 °C in a stream of chlorine containing gas. Melted anhydrous carnallite is then fed into an electrolysis cells for magnesium production, which may be connected into the flow line design, Figure 6[70]. Spent electrolyte is granulation and may be directly used as a potassium fertilizer or treated. This process was used in construction of several magnesium production plants such as Solikamsk Magnesium (SMP)[70] in Russia and Dead Sea Magnesium in Israel[72].

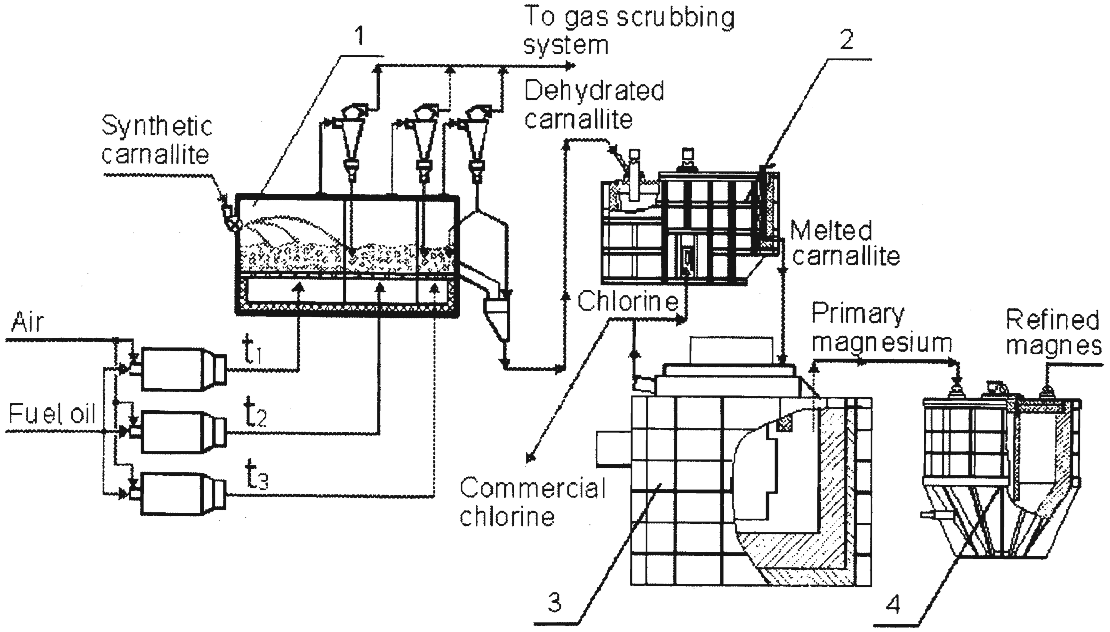

Figure 6: VAMI/STI Process.

1: Fluidzed bed furnaces, 2: Chlorinator, 3: Electrolytic cell, 4: Refining furnace

3.5: Processes Using Ammonia and Organic Reagents

The main objective of the technologies describes in this part is to reduce or eliminate the potential for unwanted hydrolysis by lowering the activity of magnesium chloride and reducing or removing the presence of moisture. Notably, ammonium chloride and magnesium chloride form a double salt, $NH_4Cl.MgCl_2.6H_2O$, which protects the magnesium chloride from being hydrolyzed during dehydration similar to carnallite. The double salt compound can be formed by the reaction of ammonia with magnesium oxides, injection of ammonia into magnesium chloride brine or by contacting the brine with an ammonium chloride solution. The double salt can be separated from the brine by cooling and can be dehydrated according to the following reactions,

$$NH_4.MgCl_2.6H_2O_{(s)} \rightarrow NH_4.MgCl_2.4H_2O_{(s)} + 2H_2O_{(g)}|^{373K} \qquad (12)$$

$$NH_4.MgCl_2.4H_2O_{(s)} \rightarrow NH_4.MgCl_2.2H_2O_{(s)} + 2H_2O_{(g)}|^{413\ K} \qquad (13)$$

$$NH_4.MgCl_2.2H_2O_{(s)} \rightarrow NH_4.MgCl_{2(s)} + 2H_2O_{(g)}|^{433K} \qquad (14)$$

$$NH_4.MgCl_{2(s)} \rightarrow NH_4Cl_{(s)} + MgCl_{2(s)}|^{509\ K} \qquad (15)$$

Application of ammonia in the production of magnesium chloride was first proposed at the beginning of the Twentieth Century and was recently used for the development of a commercial scale magnesium production smelter by Australian Magnesium Company[73]. The main advantages of the ammoniation processes are their abilities to produce magnesium electrolysis feed lower in oxides, to operate at low temperature and to deal with less corrosive materials, i.e. hot and wet HCl and Cl_2 containing gases are not involved.

3.5.1: Ammoniation of Solid Magnesium Oxide

When magnesium oxide is heated with ammonium chloride, the following reaction that produces magnesium chloride and ammonia takes place:

$$MgO_{(s)} + 2NH_4Cl_{(l)} \rightarrow MgCl_{2(s)} + 2NH_{3(g)} + H_2O(g) \qquad (16)$$

This reaction does not proceed to complete conversion of the oxides because the topological nature of the reaction products hinders contact of unreacted magnesium oxide with the molten ammonium chloride. Japanese researchers[74,75,76] described a process in the 1920's whereby fluxes such as sodium chloride and/or potassium chloride were used to considerably lower the melting point of magnesium chloride. This flux also suppressed the volatilization of the ammonium chloride and caused the complete reaction between the ammonium chloride and the magnesium oxide compound.

3.5.2: Ammoniation of Brine

In 1929, IG Farben[77] developed a process for production of anhydrous magnesium chloride by adding ammonium chloride to brine to form an anhydrous ammonium compound of magnesium chloride ($MgCl_2.6NH_3$). The brine was injected with excess ammonia to ensure saturation with ammonia. The whole system was then cooled to –30 °C to precipitate ammonium chloride. Finally, the ammoniated magnesium chloride was heated to 500 °C to produce anhydrous magnesium chloride and ammonia.

Madorsky[78] developed a process in 1969 based on the use of ammonium chloride reacting with magnesium chloride brine produced by dissolution of magnesite to form $MgCl_2.NH_4Cl.6H_2O$ at 100 °C as follows:

$$MgCO_{3(s)} + 2HCl_{(aq)} + NH_4Cl_{(aq)} + 5H_2O_{(l)} \rightarrow MgCl_2.NH_4Cl.6H_2O_{(s)} + CO_{2(g)} \quad (17)$$

The double salt was heated at 800 °C in a flash dryer to produce anhydrous magnesium chloride.

Christensen et al.[79] from Dow Chemical Company described a process in 1963 whereby magnesium chloride was fed into an ammonia solution instead of injecting ammonia into magnesium chloride brine. They claimed this method resulted in less oxide formation. Magnesium chloride hexa ammoniate was then precipitated and separated at -10 °C and magnesium chloride and ammonia were recovered by heating this compound at 400 °C.

Goodenough and Gaska from Dow Chemical Company[80,81] developed a similar process in 1963 to 1966 for the production of anhydrous magnesium chloride. Their process comprised adding magnesium chloride to an agitated aqueous ammonia solution containing not more than 65 wt% ammonia, maintaining the ammonia concentrate in the mixture at between 35 to 65 wt% throughout the reaction at the temperature of 40 to 75 °C, separating the precipitated magnesium chloride hexa-ammoniate from the reaction mixture at -10 to 20 °C and heating the mixture to produce anhydrous magnesium chloride with an assay of 99.8 wt%.

Goodenough and Gaska[82] from Dow Chemical Company described another process in 1966 for dehydration of $MgCl_2.NH_4Cl.6H_2O$ by blowing nitrogen into a reactor at 135 to 178 °C to produce anhydrous magnesium chloride ammoniate followed by final dehydration of this compound to produce anhydrous magnesium chloride at 345 to 385 °C.

J. Macey et al.[83,84] developed a process in 1972 and 1973 for the production of anhydrous magnesium chloride from concentrated and purified brine from the Great Salt Lake of Utah by contacting magnesium chloride brine with strong ammonium chloride at 110 °C. The reaction products were cooled to ambient temperature to precipitate $NH_4Cl.MgCl_2.6H_2O$. The precipitated double salt was separated and washed with ammonium chloride and dehydrated in two stages to $NH_4Cl.MgCl_2$ in a rotary dryer. Anhydrous $MgCl_2.NH_4Cl$ was then fed into two brick lined chambers, one for the decomposition of the anhydrous magnesium chloride ammonium and the other for the cleaning of molten magnesium chloride maintained at 844 °C. The ammonia was collected from the first chamber and conducted to water scrubbers.

In 1974, Suzukawa et al.[85] form Ube Industries Ltd. developed another method for dehydration of $MgCl_2.NH_4Cl.6H_2O$ in an atmosphere of anhydrous ammonia to produce $MgCl_2.NH_4Cl.3.5H_2O$ at 300 °C. The $MgCl_2.NH_4Cl$ that was produced was then charged to a decomposition furnace to produce anhydrous magnesium chloride at 800 °C. They claimed that dehydration in an atmosphere of ammonia minimized the risk of hydrolysis.

3.5.3: Ammoniation with Application of Ethylene Glycol

Hydrolysis of magnesium chloride tends to occur in the last stages of dehydration of ammoniated magnesium chloride. To eliminate the risk of oxide formation, dehydration can be performed in an ammonia-enriched atmosphere. Another means to avoid this problem is to use an organic compound like ethylene glycol, which makes strong bonds with ammonium and magnesium chloride, and provides the possibility of water removal without hydrolysis.

Bott et al.[86] from Nalco Chemical Company developed the so called "Nalco-Freeport" process in 1971 for the production of organolead compounds by the electrolytic decomposition of a sacrificial lead anode utilizing a mixture of anhydrous oxygenated solvents consisting of diethylether tetraethylene glycol (DETEG) and tetrahydrofuran (THF) as well as the production of anhydrous magnesium chloride as a byproduct. The process consisted of the treatment of magnesium chloride brine with anhydrous ammonia to form $MgCl_2.xNH_3$ where x = 1 to 6, separating the ammine complex from the solvent mix and decomposing the ammine under water free conditions by heating at 300 to 400 °C for 10 to 16 hours to drive off the ammonia and recovering the consequently freed anhydrous $MgCl_2$, Reaction 18.

$$2RMgCl_{(org)} + 2R'Cl_{(org)} + Pb_{(s)} \rightarrow (RR')_2Pb_{(org)} + 2MgCl_{2(s)} \qquad (18)$$

where R and R' are lower alkyl alkalines.

Allain et al., also from Nalco[87,88,89,90], described a process in series of patents from 1976 to 1980 for the production of anhydrous magnesium chloride from hydrates consisting of dissolving magnesium chloride hydrates in diethyl ether tetraethylene glycol (DETEG) to form a magnesium chloride hydrate solution containing $MgCl_2$ combined with 3 moles of ethylene glycol, heating this solution to remove all the water to produce an anhydrous ethylene glycol magnesium chloride solution at 205 °C, treating the water free magnesium chloride ethylene glycol solution with ammonia to form a magnesium chloride ammonia complex which was precipitated from the ethylene glycol at -15 to 50 °C; removing the precipitate from the ethylene glycol and washing it with a low boiling solvent such as tetrahydrofuran to remove any ethylene glycol entrained in the precipitate and heating the magnesium chloride ammonia complex to drive off the ammonia at 300 to 400 °C. These steps produced magnesium chloride with 0.8 wt% oxide content.

Amundsen et al.[91] from Norsk Hydro developed a process in 2000 consisting of selective calcination of magnesium containing minerals in the range from 350 to 900 °C, selective leaching of magnesium from such calcines using ammonium chloride dissolved in a substantially water-free, polar, organic ethylene glycol media; separation of the impurities; precipitation of magnesium chloride hexa ammoniate by treating the solution with an excess amount of ammonia in a crsytallyzer prior to the dehydration, separation of magnesium chloride hexa ammoniate by filtration; centrifuging and finally thermal decomposition of ammoniated magnesium chloride to produce magnesium chloride.

Sheehan et al.[92] from CSIRO described a process in 2000 in which hydrated magnesium chloride was mixed in a vessel with ethylene glycol. The mixture was dehydrated in distillation columns with the addition of anhydrous ammonia gas to the crytallyzer. A slurry of magnesium chloride hexa-ammoniate was continuously pumped from the crsytallyzer into a pressure filter where the crystals were washed with methanol saturated with ammonia. The crystals were transported to a fluidized bed calciner where methanol was evaporated from the crystal at 120 °C and followed by final calcination to produce anhydrous magnesium chloride at 450 °C, Figure 7. This process was used for the design of the Stanwell magnesium smelter[93].

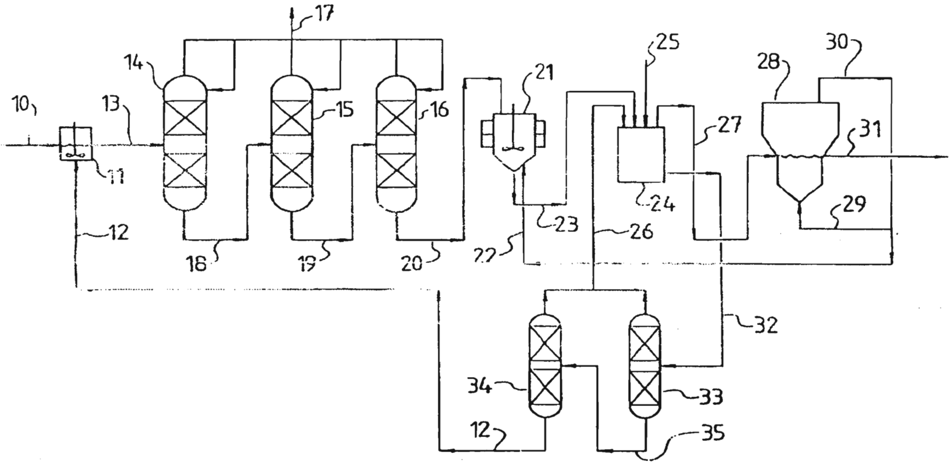

Figure 7: Sheehan's Process Flow Diagram.

10: Magnesium Chloride Brine, 11: Mixer, 12: Ethylene glycol, 14-15-16: Distillation Columns, 21: Crystallizer, 23: Magnesium chloride hexa-ammoniate, 26: Ammonia, 28: Fluidized Bed Calciner

3.5.4: Ammoniation with Application of Alcohols

Sivilotti et al. from ALCAN Ltd.[93,94] developed a process in 1994 and 1996 whereby an aqueous solution of magnesium chloride was reacted with ammonium chloride saturated with a very low boiling point alcohol (methanol and/or ethanol) at 10 to 60 °C while maintaining saturation with ammonia. The ammoniated magnesium chloride $MgCl_2.6NH_3$ was precipitated, separated and heated at 600 °C to produce anhydrous magnesium chloride with 0.33 % MgO and ammonia, Figure 8.

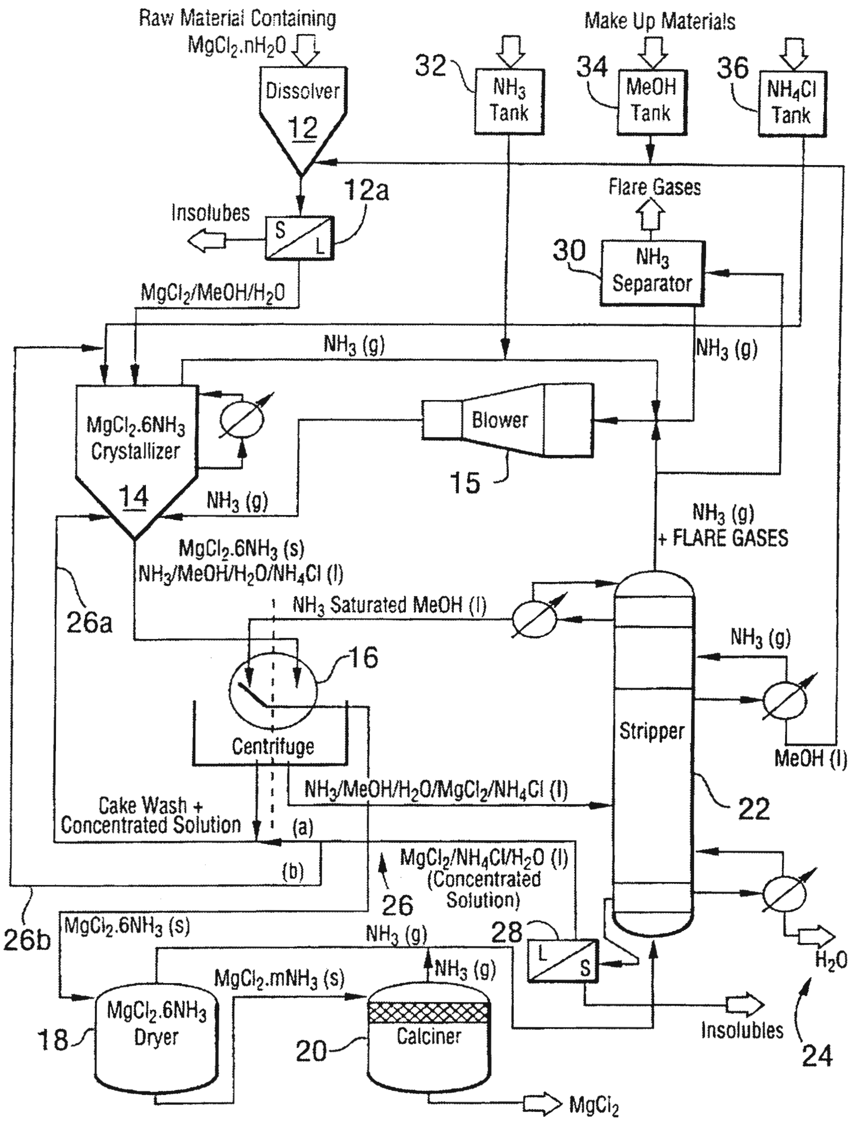

Figure 8: ALCAN Process Flow Diagram.

10: Brine Tank, 11: Spray Dryer, 12: Dissolver, 14: Crystallizer, 16: Centrifuge, 18: Dryer, 20: Calciner

3.5.5: Application of Organic Reagents

The use of organic reagents such as amyl and amines, which make strong bonds with magnesium chloride provides the possibility of safe removal of water and was pursued for the development of new anhydrous $MgCl_2$ feed preparation processes. In particular, Belchetz[95] from MW Kellogg Company proposed a process in 1945 whereby brine was contacted with isoamyl alcohol. This alcohol has a boiling point of 130 °C and the brine was mostly immiscible in the alcohol. Drying distillation of the resulting solution, water was first removed and the alcohol was then separated and recycled in the process.

Dow Chemical Company[96] described a similar process in 1966 comprising contacting magnesium chloride hydrates with a NN-dialkyl amide solvent such as NN-dimethyl formamaide to form a complex of the two, distilling away the water at 100 to 200 °C and then distilling away the organic reagent at 200 to 450 °C.

Dow Chemical Company[97] extended the process in 1969 by adding a cycloaliphatic ether, such as tetra hydofuran, to a liquid monohydric alkanol solution such as magnesium chloride hydrates dissolved in ethanol. A complex containing both the alcohol and ether was formed at room temperature. Upon heating at 80 to 90 °C and then at 200 to 300 °C the alcohol and the ether were removed and magnesium chloride was produced.

Dolezal[98] proposed a process in 1976 comprising contacting magnesium chloride hydrates or magnesium chloride brine with a hydrochloride of an amine of the class consisting of diethyl amine of triethylamine at 100 °C. The complex that was formed was then heated at 180 °C to drive off water leaving the anhydrous complex of amine and magnesium chloride. Further heating at 250 to 320 °C resulted in decomposition of complex and the production of anhydrous magnesium chloride.

3.6: Processes Based on Analytical Methods

Several processes for the production of anhydrous magnesium chloride based on analytical methods with the potential for limited industrial application in primary magnesium production have been developed. Some of these methods were used in the preparation of magnesium chloride catalysts. Albizzati et al.[99] developed a method in 1977 for the production of beta magnesium chloride with improved catalytic properties. This phase was prepared from magnesium chloride hexahydrate in a two-stage dehydration process by first contacting the magnesium chloride hexahydrate with thionyl chloride at 25 to 60 °C for 40 hours to produce magnesium chloride dihydrate followed by another dehydration procedure at 95 °C for another 32 hours to produce crystalline beta magnesium chloride. Albizzati et al.[100] also synthesized the beta phase of magnesium chloride in 1983 by prolonged reaction of $SOCl_2$ with hydrated $MgCl_2$, in particular $MgCl_2.6H_2O$ or $MgCl_2.2H_2O$, at a temperature ranging from room temperature up to the boiling point of $SOCl_2$, i.e., 25 to 60 °C, for 40 hours. The objective of their invention was to provide a new crystalline form of $MgCl_2$ which was used as a support or a carrier in a catalyst capable of remarkably boosting the yield of polymer in grams /grams of Ti (or other transition metal).

Bull[101] described a process in 2002 for the chlorination of magnesia and magnesite with carbon tetrachloride and phosgene, which occurs at 500 to 600 °C. Bull stated that this process does not have difficulties of the high temperature chlorination process and can be applied to magnesite in a rotary reactor. Reactions 19 and 20 describe the process.

$$MgO_{(s)} + CCl_{4(g)} = MgCl_{2(s)} + COCl_{2(g)} \tag{19}$$

$$MgO_{(s)} + COCl_{2(g)} = MgCl_{2(s)} + CO_{2(g)} \tag{20}$$

In 2002, Sharma[102] described a process whereby anhydrous $MgCl_2$ was prepared by dissolving magnesite in a starting melt of $MgCl_2$-$CeCl_3$, thereby forming $MgCl_2$, CeOCl and CO_2. The CeOCl was converted back to $CeCl_3$ by chlorination with Cl_2 in the presence of a reducing agent such as CO_2 or H_2 to yield a melt of $MgCl_2$-$CeCl_3$ having a higher concentration of $MgCl_2$. These steps were repeated to further increase the concentration of $MgCl_2$. The concentrated $MgCl_2$-$CeCl_3$ melt was then reacted with MgO and Cl_2 in the absence of a reducing agent to convert the dissolved $CeCl_3$ into an insoluble CeO_2 precipitate that could be separated to yield pure $MgCl_2$.

3.7: New Developments

It has been reported that the preparation of acceptable feed containing little or no magnesium oxide contributes fifty percent of the cost of electrolytic magnesium production[106]. If the suspended oxides could be dissolved rather than being present as a solid phase, then the feed with magnesium oxide as an impurity could be used without the unwanted sludge formation. Furthermore, if a new electrolyte that can dissolve sufficient magnesium oxide and allow this dissolved magnesium oxide to be decomposed electrolytically into magnesium and oxygen, then magnesium oxide in place of magnesium chloride could be used as a feed material. In that instance, an entirely new process, different from the present electrolytic magnesium production process and similar to the Hall Heroult process of aluminum production, could be developed. Research is exploring processes based on this idea.

Sharma[103] developed a process in 1994 whereby magnesium is produced using a solution of MgO in a molten mixture of $NdCl_3$ and $MgCl_2$ as the electrolyte. This process requires 12,200 kJ/kg Mg as compared to 20,100 kJ/kg for the Dow process. The high cost of $NdCl_3$ and production of magnesium with an admixture of neodymium are likely to be drawbacks of this method.

Sharma[104] developed another process in 1997 whereby a melt with high magnesium oxide content is reacted with a gas having equi-molar ratio of hydrogen and the chlorine a temperature of 725 to 800 °C to produce anhydrous magnesium chloride. This was followed by the electrolysis of the produced magnesium chloride to magnesium and recycling of chlorine from the anode.

In a variation of this approach, Sharma[105] described a process in a 1989 patent in which partially dehydrated magnesium chloride contaminated with magnesium oxide was reacted with an electrolyte consisting of magnesium, lithium and/or calcium cations and fluorine and chlorine anions. The magnesium chloride and/or magnesium oxide reacted with and dissolved in the electrolyte and the lithium and calcium metal initially produced electrochemically and transiently at the cathode reacted chemically with magnesium cations in the electrolyte to produce magnesium metal. Thus, the method essentially involved a first electrochemical step to produce lithium or calcium metal and a subsequent second chemical step in which lithium and calcium reacted with magnesium fluoride in the electrolyte to produce magnesium metal[106].

3.8: Conclusions

The present overview of the many different anhydrous magnesium chloride production technologies shows that, despite the large number of patents, only a limited number of distinct ideas have been discovered but were repeatedly used by different ventures in sufficiently different garb to warrant the issuing of patents. It is also well known that recent severe competition combined with the challenges of starting up novel and complex processes has resulted in very costly consequences for some commercial ventures, Magnola Metallurgie Inc. and Australian Magnesium Corporation, in particular.

Table I summaries the main distinct technologies presented in this review and cites the name of the developing company, the main advantages and disadvantages and the location where the technology is, was or was anticipated to be used, if at all.

The recent, but anticipated temporary sharp decline in the price of magnesium caused by the Chinese supply of low cost magnesium produced by thermal reduction methods, has forced many north American and European manufacturers out of the magnesium production business, notably Timinco Ltd and Northwest Alloys. The only businesses surviving this severe competition at the time of writing were Norsk Magnesium in Quebec, USMag in Utah and the carnallite based technologies being practiced in several former Soviet Unions countries and in Dead Sea Magnesium. Norsk Magnesium's technology is not available for sale or license to other potential magnesium producers and though the carnallite based technology is purchasable though VAMI/STI, it is not easily applicable to many magnesium resources. This commercial situation means that all prospective magnesium producers must develop their own feed production processes whenever the VAMI/STI carnallite technology cannot be used.

It seems inevitable that there will eventually be the development of a new feed preparation processes in response to the increasing demand for magnesium given the global commitment to protect the environment but it is also clear that this field requires fundamental studies and validation of some the basic kinetic and mass transfer principals, which would provide the basis for the development of new commercial viable processes.

Table I: Major Anhydrous Magnesium Chloride Production Technologies.

Technology	Technology Developer	Advantages	Disadvantages	Practice
Suppression of hydrolysis reactions [2.21.1]	Norsk Hydro [23,24,25]	• Proven technology • Considerable level of process automation • Fine control of cell chemistry • Production of marketable byproduct	• Technology is not available for sale • High energy consumption • Large amounts of HCl recirculation • Strict requirement for sealed operation	Becancour, Quebec
Bone dry dehydration of hydrates and back chlorination of oxides [2.21.2]	Shell International [27,28]	• Simplicity of operation • Low energy consumption	• Process never been practiced at industrial scale • Operation of shelf type dryer in a corrosive environment	None
Dehydration of hydrates with fused salts [2.21.4]	Dow Chemical Company[5]	• Fine control of temperature and amperage selection due to the excess cooling effect of the moisture in the cell • Low feed preparation cost because of absence of chlorination & dehydration processes	• Anode gas is hardly marketable • Complicated cell operation • Large amounts of sludge formation • High anode-graphite consumption • Low current efficiency • High operating cost	Freeport, Texas (Not operational)
Hydrochlorination of molten salts [2.21.5]	Magnola Metallurgie [45]	• Low preliminary dewatering costs	• Mechanical complexity • Complex processs optimization • High operating costs	Danville, Quebec (Not operational)
Carbochlorination of magnesium oxides [2.21.6]	MagCorp (US Mag)[5]	• Low feed preparation cost • Process flexibility	• Batch process • High operating costs	Rowley, Utah
Carnallite Process [2.21.7]	VAMI/STI [70,71]	• Proven technology • Availability of technical support • Considerable level of process automation • Fine control of cell chemistry	• Only treats carnallite: $KCl.MgCl_2.6H_2O$ • Produces large amounts of potassium chloride as a byproduct	Dead Sea Magnesium (DSM), Israel & several CIS plants
Ammoniation with application of ethylene glycol [2.22.3]	CSIRO[92]	• Production of high purity anhydrous magnesium chloride • Recycle of effluents	• Process is under development	Stanwell, Queensland (Not operational)
Ammoniation with application of alcohols [2.22.4]	ALCAN[93,94]	• Production of anhydrous magnesium chloride • Recycle of effluents	• Process is under development	None

3.9: References

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Chapter 4: Thermochemical Analysis of the Production of Anhydrous $MgCl_2$

Many researchers have studied the dehydration and hydrolysis of magnesium chloride under equilibrium conditions[3,4,5,6,7,8,9,10]. It is known that magnesium chloride is very hygroscopic and for this reason it is hard to handle in normal atmosphere due to the pickup of moisture. It is also know to be very susceptible to hydrolysis and for this reason, it is difficult to produce anhydrous magnesium chloride by thermal dehydration. Figure 9 shows that the magnesium chloride hydrates precipitated from aqueous solutions contain, depending on temperature, 12, 8, 6, 4, 2, or 1 molecules of water of crystallization[1,2]. Figure 9 also shows that each hydrate exists only over a definite temperature range. Above 0 °C, only 6 molecules of water or less appear in the crystalline phases and these are of commercial importance for the production of anhydrous $MgCl_2$.

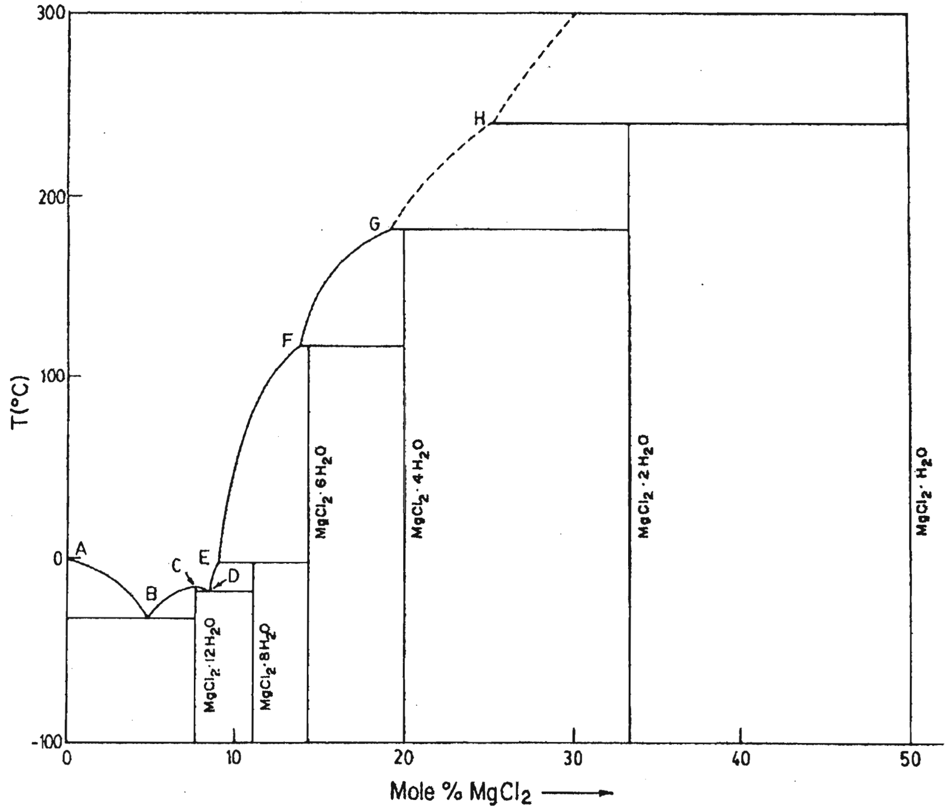

Figure 9: Water-rich Portion of the $MgCl_2$ - H_2O Phase Diagram[1,2].

In the sections that follow, thermodynamic data available in the literature have been examined, expressions for the Gibbs Energy as a linear function of temperature have been developed and the equilibrium partial pressure of water vapour in equilibrium with pairs of oxides has been plotted. Predominance Area Diagrams (aka Kellogg Diagrams) are included to provide a map of the equilibrium behaviour of the system based on available data and a discussion of the equilibrium behaviour of the system is included.

4.1: Dehydration of $MgCl_2.6H_2O$ to $MgCl_2.2H_2O$

Dehydration of $MgCl_2.6H_2O$ to $MgCl_2.2H_2O$ is shown in Reactions 21 and 23. Figure 10 and Figure 11 display the equilibrium partial pressure needed for the hydrates to co-exist.

$$MgCl_2{\cdot}6H_2O_{(s)} \leftrightarrow MgCl_2{\cdot}4H_2O_{(s)} + 2H_2O_{(g)} \tag{21}$$

$$\Delta G^{0}_{(1)}\Big|^{390K}_{298K} = 232158 - 548.92T \ \left(J/_{mole}\right)^{8} \tag{22}$$

$$MgCl_2{\cdot}4H_2O_{(s)} \leftrightarrow MgCl_2{\cdot}2H_2O_{(s)} + 2H_2O_{(g)} \tag{23}$$

$$\Delta G^{0}_{(2)}\Big|^{455K}_{298K} = 269062 - 580T \quad \left(J/_{mole}\right)^{8} \tag{24}$$

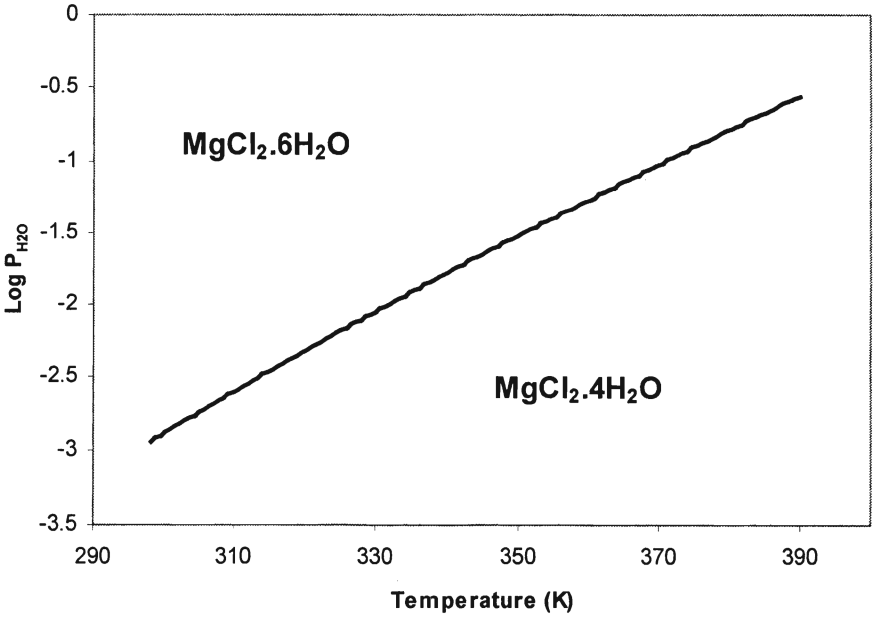

Figure 10: Water Vapor Equilibrium Partial Pressure for Reaction 21 as a Function of Temperature.

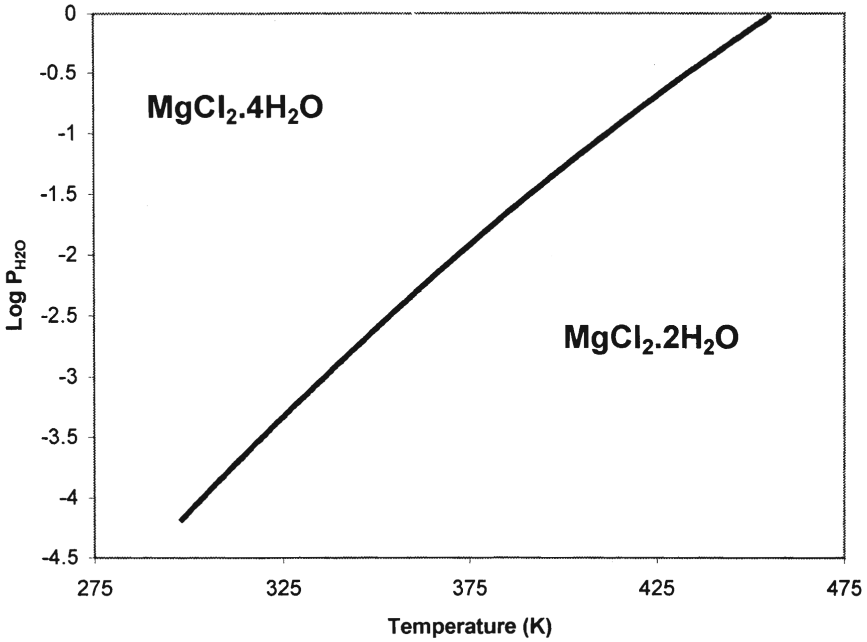

Figure 11: Water Vapor Equilibrium Partial Pressure for Reaction 23 as a Function of Temperature.

It can be seen that under equilibrium conditions, the dehydration of magnesium chloride hexahydrate to magnesium chloride dihydrate is possible without significant hydrolysis. For dehydration to occur, the P_{H2O} surrounding the hydrate must be less than the equilibrium P_{H2O}. This can be accomplished by increasing the temperature, which increases the equilibrium P_{H2O}, being careful not to increase the temperature above the melting point of the hydrate or the latter melts congruently in its own waters of crystallization, rendering any additional dehydration difficult[1,9].

4.2: Dehydration of $MgCl_2.2H_2O$ to $MgCl_2.H_2O$

Dehydration by heating beyond the dihydrate requires special precautions and simple heating without an HCl atmosphere leads to hydrolysis. There are disagreements between researchers regarding the composition of the products but one possible outcome is the formation of MgOHCl, Reactions 25 and 27. Figure 12 presents the Gibbs free energy change for the dehydration of the dihydrate, the hydrolysis of the $MgCl_2$ and the decomposition of the MgOHCl as a function of temperature. The figure does not clearly show the thermodynamic conditions necessary to suppress hydrolysis while permitting dehydration.

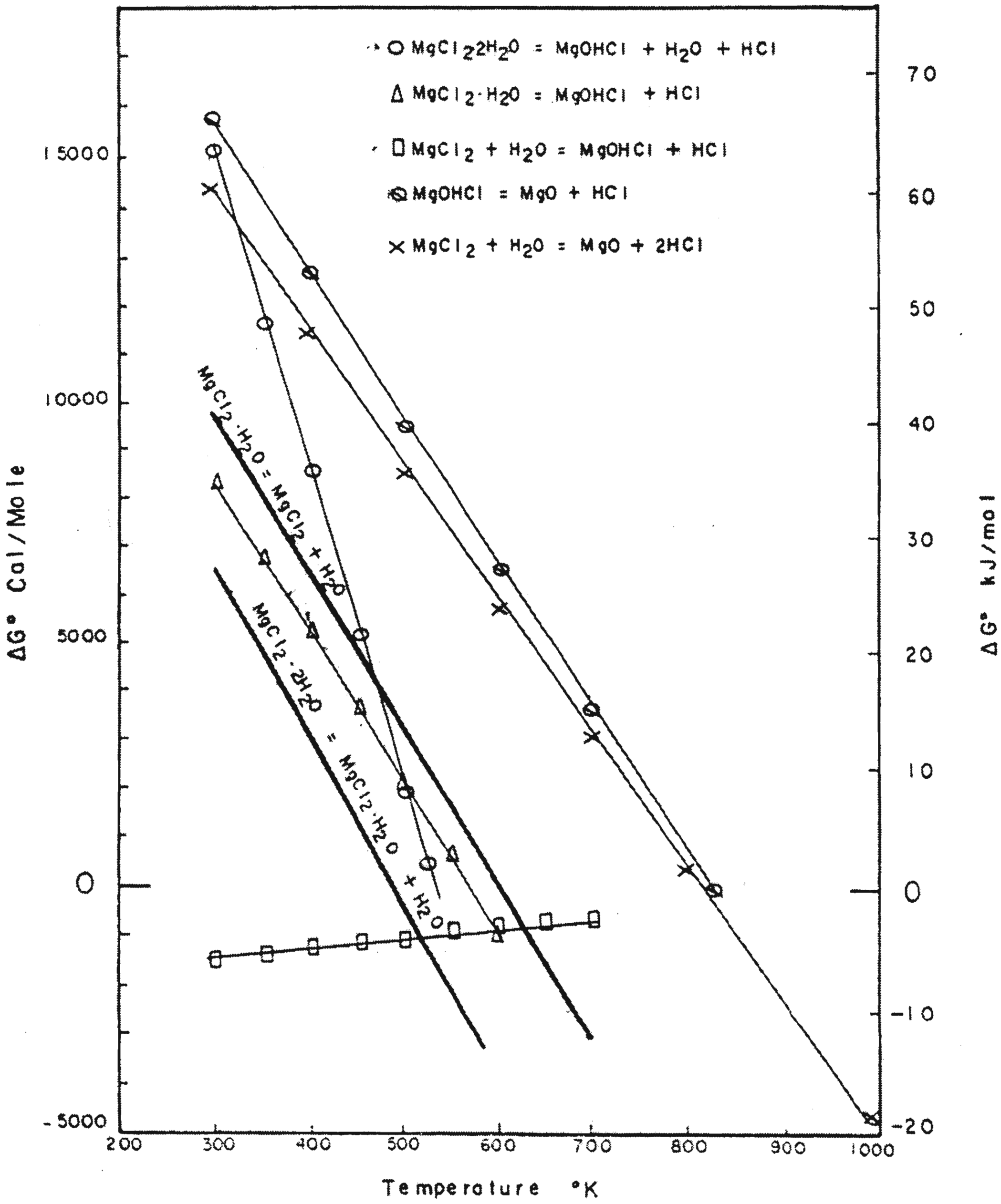

Figure 12: Gibbs Energy Change for Reactions that can occur during $MgCl_2.2H_2O$ Dehydration[1,2].

Kelly[8] claimed that the dihydrate reduced to the monohydrate prior to complete dehydration as shown in Reaction 25. In addition, he saw that the hydrolysis reaction, Reaction 27, occurred at the same time. Figure 13 and Figure 14 display the equilibrium water vapour partial pressure needed for Reactions 25 and 27 to occur[1,2,8].

$$MgCl_2 \cdot 2H_2O_{(s)} \leftrightarrow MgCl_2 \cdot H_2O_{(s)} + H_2O_{(g)} \tag{25}$$

$$\Delta G^0_{(5)}\Big|^{513K}_{298K} = 70256 - 143.02T \left({}^{J}\!/_{mole} \right)^{8} \tag{26}$$

$$MgCl_2 \cdot 2H_2O_{(s)} \leftrightarrow MgOHCl_{(s)} + H_2O_{(g)} + HCl_{(g)} \tag{27}$$

$$\Delta G^0_{(6)}\Big|^{823K}_{298K} = 143764 - 272.88T \left({}^{J}\!/_{mole} \right)^{8} \tag{28}$$

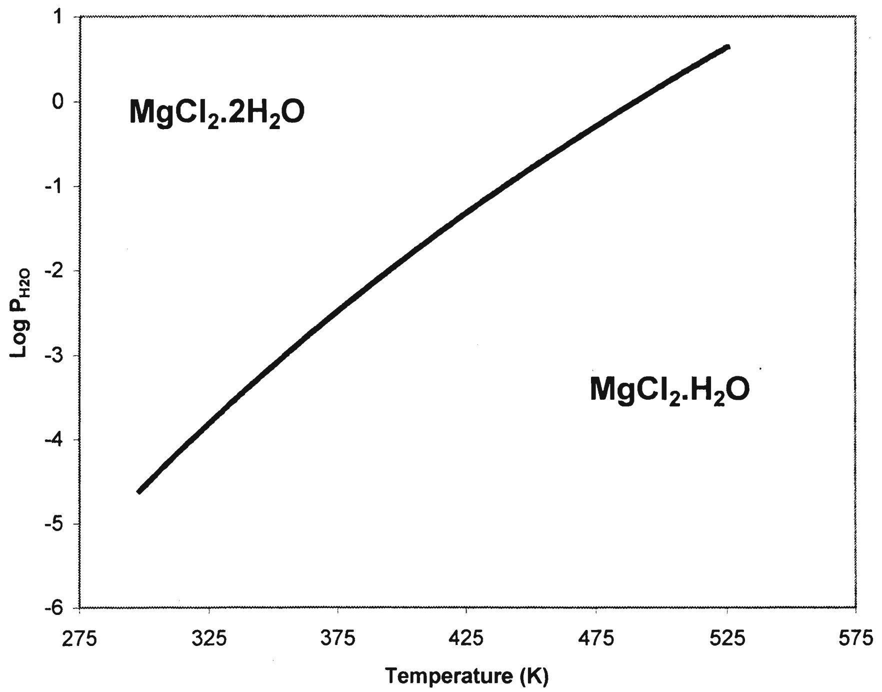

Figure 13: Water Vapor Equilibrium Partial Pressure for Reaction 25 as a Function of Temperature.

Reaction 27 is inhibited by the vapor pressure of water generated by Reaction 25, which occurs simultaneously. Hydrolysis can be prevented by the use of HCl according to Le Chatelier's Principle provided that the local partial pressure of HCl gas exceeds the value calculated for Reaction 27.

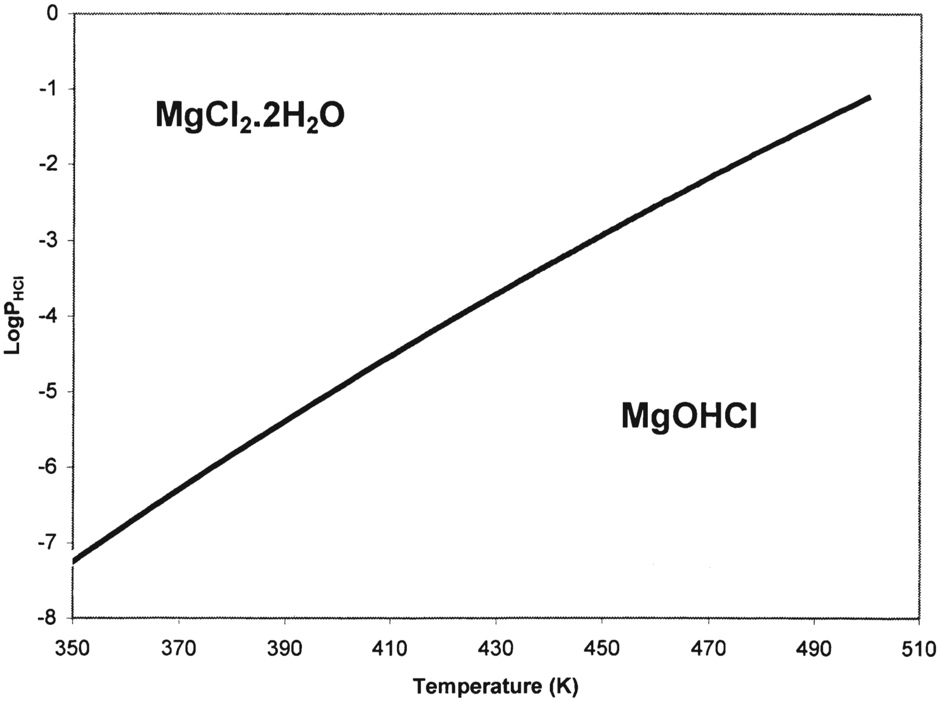

Figure 14: HCl Equilibrium Partial Pressure for Reaction 27 as a Function of Temperature.

4.3: Dehydration of $MgCl_2.H_2O$ to $MgCl_2$

The final stage in dehydrating magnesium chloride hexahydrate is to remove the last water of crystallization from the monohydrate, Reaction 29. The hydrolysis of the monohydrate to form hydroxychloride occurs at a higher P_{HCl} as compared to the hydrolysis of the dihydrate. Figure 15 and Figure 16 display the equilibrium partial pressures of H_2O and HCl needed for the hydrates to co-exist. It becomes obvious that a high P_{HCl} is required to prevent hydrolysis to form MgOHCl, Reaction 31.

$$MgCl_2{\cdot}H_2O_{(s)} \leftrightarrow MgCl_{2(s)} + H_2O_{(g)} \qquad (29)$$

$$\Delta G^0_{(9)}\Big|_{298K}^{823K} = 82235 - 138.35T \left(J/_{mole}\right)^{[8]} \qquad (30)$$

$$MgCl_2{\cdot}H_2O_{(s)} \leftrightarrow MgOHCl_{(s)} + HCl_{(g)} \qquad (31)$$

$$\Delta G^0_{(11)}\Big|_{298K}^{823K} = 73650 - 130.13T \left(J/_{mole}\right)^{[8]} \qquad (32)$$

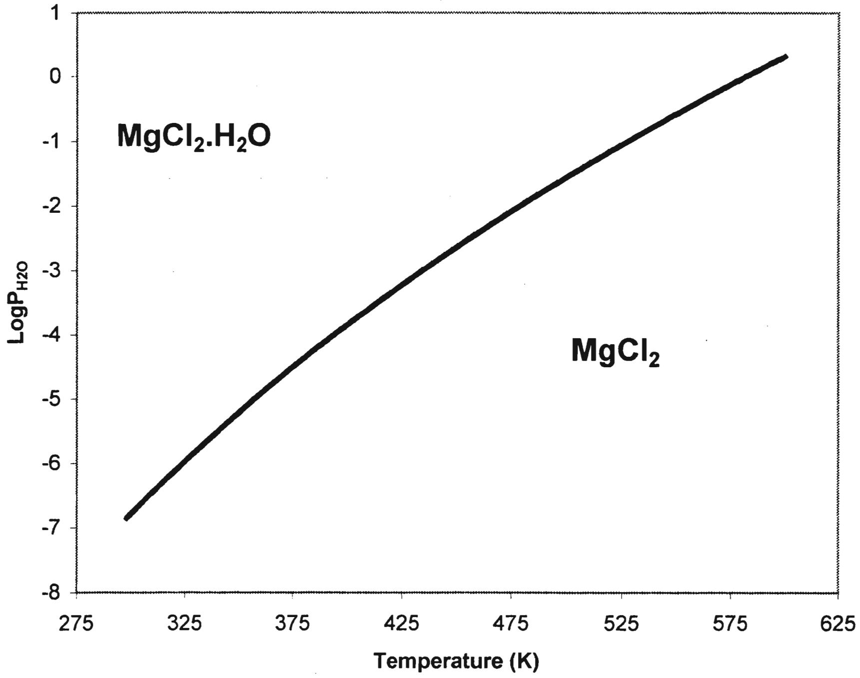

Figure 15: Water Vapor Equilibrium Partial Pressure for Reaction 29 as a Function of Temperature.

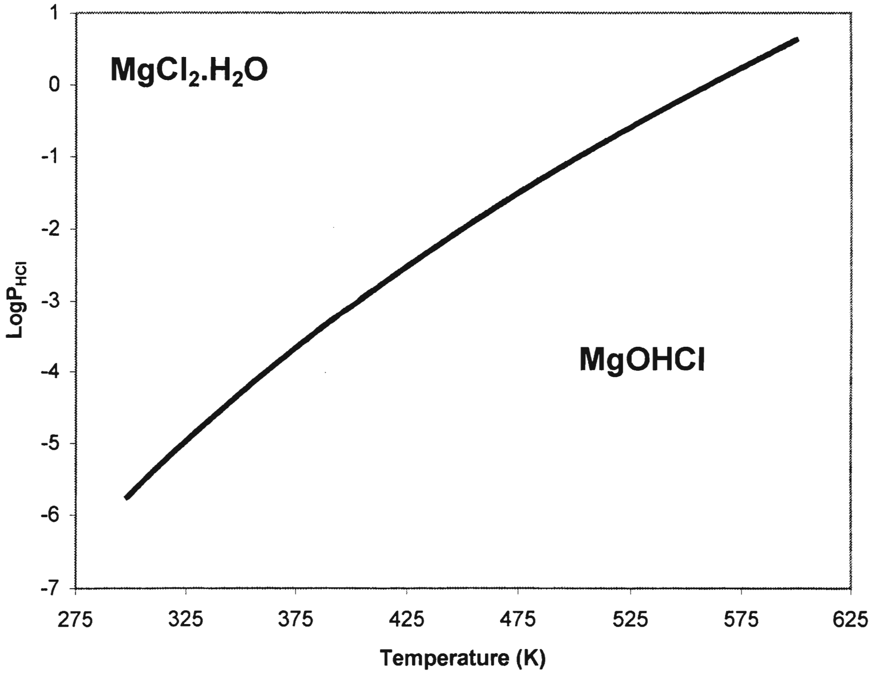

Figure 16: HCl Equilibrium Partial Pressure for Reaction 31 as a Function of Temperature.

4.4: Predominance Area Diagrams

As presented in Figure 12, the plot does not clearly show the conditions to suppress hydrolysis while at the same time permitting dehydration, if such is possible under the conditions in effect. Therefore, it is desirable to construct predominance area diagrams, also called Kellogg diagrams, of the Mg-Cl-H-O system. Construction of predominance area diagrams was thought useful to determine which reactions are occurring in this system.

The construction of the predominance area diagrams was performed using FactSage^{TM}. Because the system being considered has four components, it is necessary to specify a thermodynamic parameter so that the diagram can be plotted with just two degrees of compositional freedom, i.e., P_{HCl} and P_{H2O}. To this end, the partial pressure of Cl_2 in equilibrium with the components of $MgCl_2.6H_2O$ was determined at each of the temperatures considered in the plots below using the "Equilib" application in FactSage^{TM} coupled with the Fact Solid and Pitzer databases. It can be seen that the calculated P_{Cl2} ranged from $6.13x10^{-13}$ atm at 473K to $3.98x10^{-7}$ atm at 873K. It was found that varying the partial pressure of chlorine gas over the present range did not alter the positions of the boundaries in the plots, except for the $Mg(OCl_4)_2(H_2O)_6$ region which increased in size with increasing P_{Cl2}. Also, the 1 atm isobar was seen to move to higher values of P_{HCl} for P_{HCl} less than 0.001 atm as P_{Cl2} was varied over the present range.

Figures 17 to 21 show predominance area diagrams for the Mg-O-H-Cl system at various temperatures. The following observations can be made from Figures 17 to 21. .

- At 473 K $Mg(OH)_2$ is the stable phase at $P_{H2O} = 1$ atm. Increasing dehydration temperature shifts this phase stability area to larger values of P_{H2O}. Therefore, $Mg(OH)_2$ is an important phase to consider in the hydrolysis at low dehydration temperatures and high values of P_{H2O}.

- At 473 K, $MgCl_2.6H_2O$ cannot coexist with MgOHCl and dehydration of $MgCl_2.6H_2O$ to $MgCl_2.4H_2O$ can proceed without evolution of HCl and significant hydrolysis, Reaction 21. Equilibrium P_{H2O} needed for the hydrates to co-exist is about 10 atm and for dehydration to occur, the P_{H2O} surrounding the hydrate must be less than the equilibrium P_{H2O}.

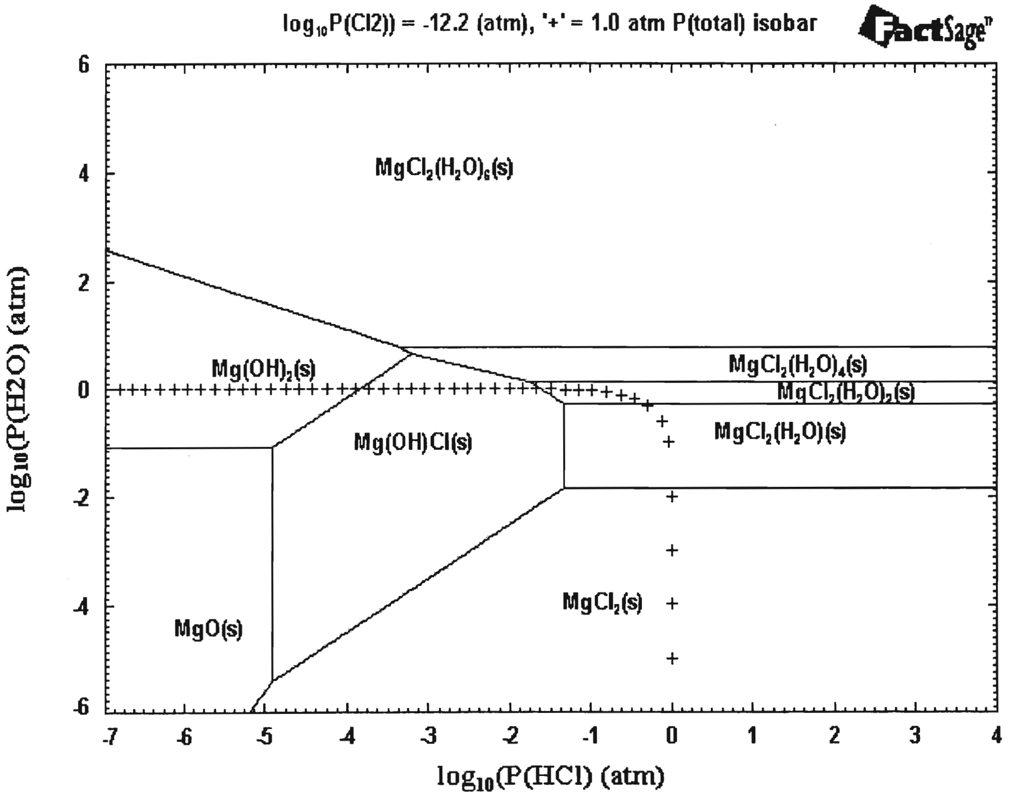

Figure 17: Predominance Diagram of Mg-Cl-O-H System, 473 K. ($P_{Cl2} = 6.3 \times 10^{-13}$).

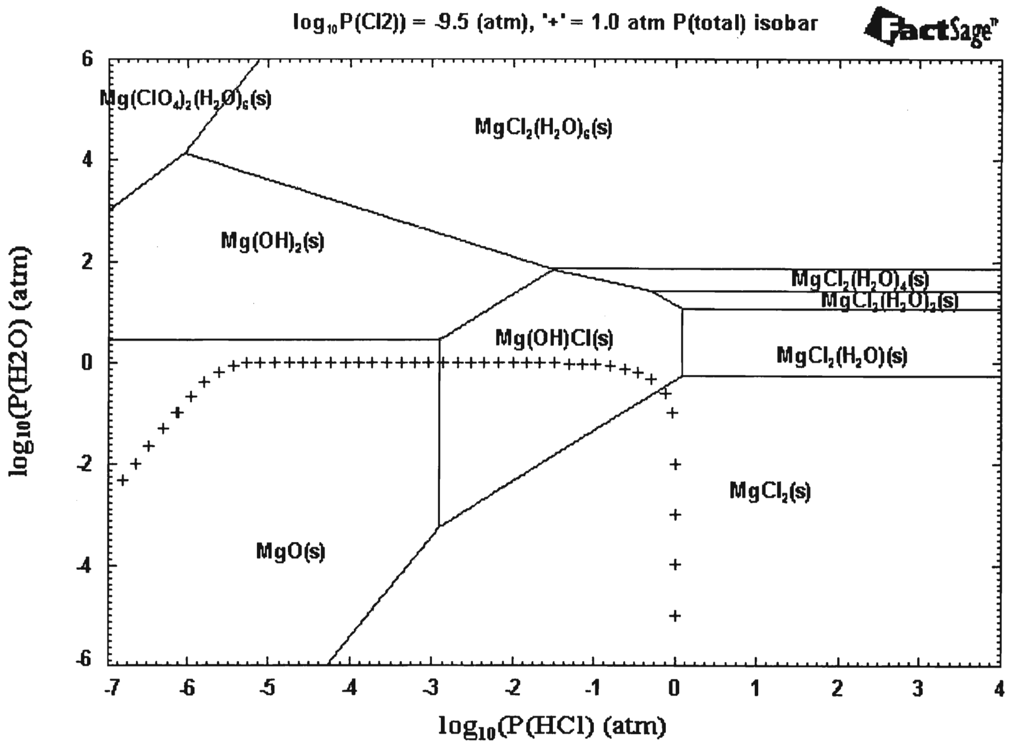

Figure 18: Predominance Diagram of Mg-Cl-O-H System, 573 K($P_{Cl2} = 3 \times 10^{-10}$).

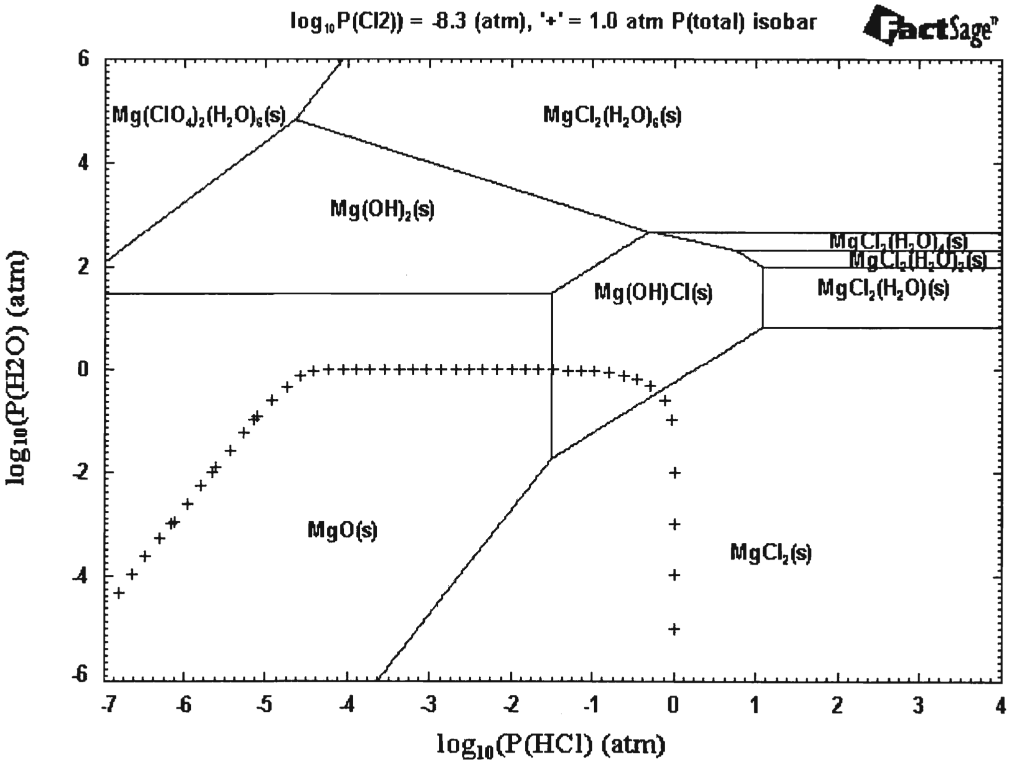

Figure 19: Predominance Diagram of Mg-Cl-O-H System, 673 K $P_{Cl2} = 5 \times 10^{-9}$).

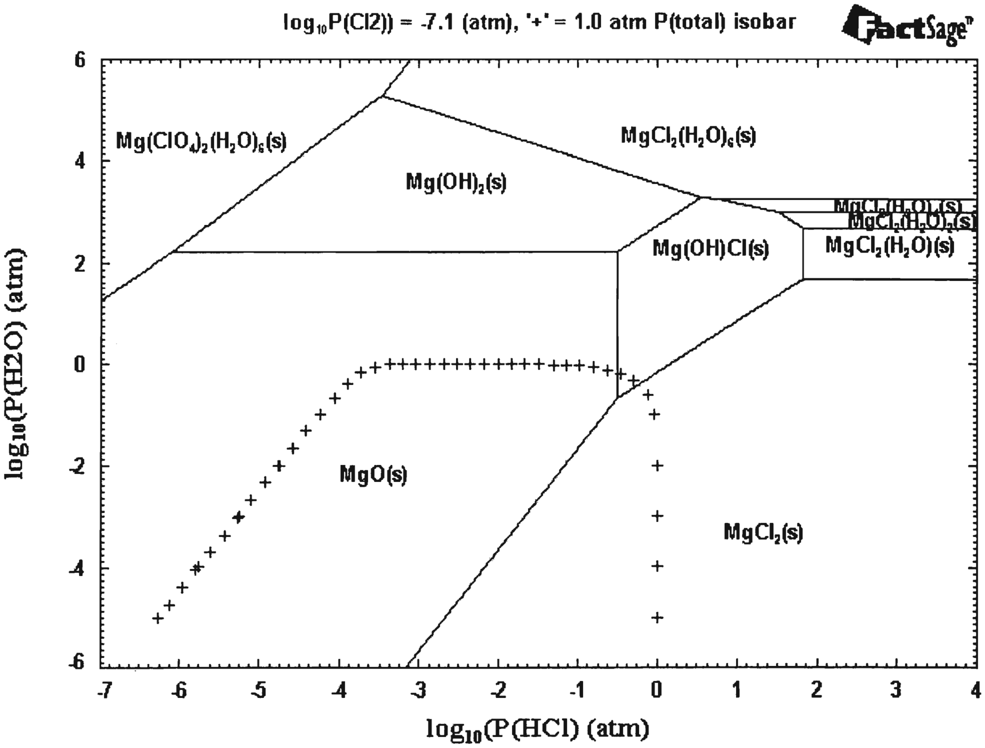

Figure 20: Predominance Diagram of Mg-Cl-O-H System, 773 K $P_{Cl2} = 7.94 \times 10^{-8}$).

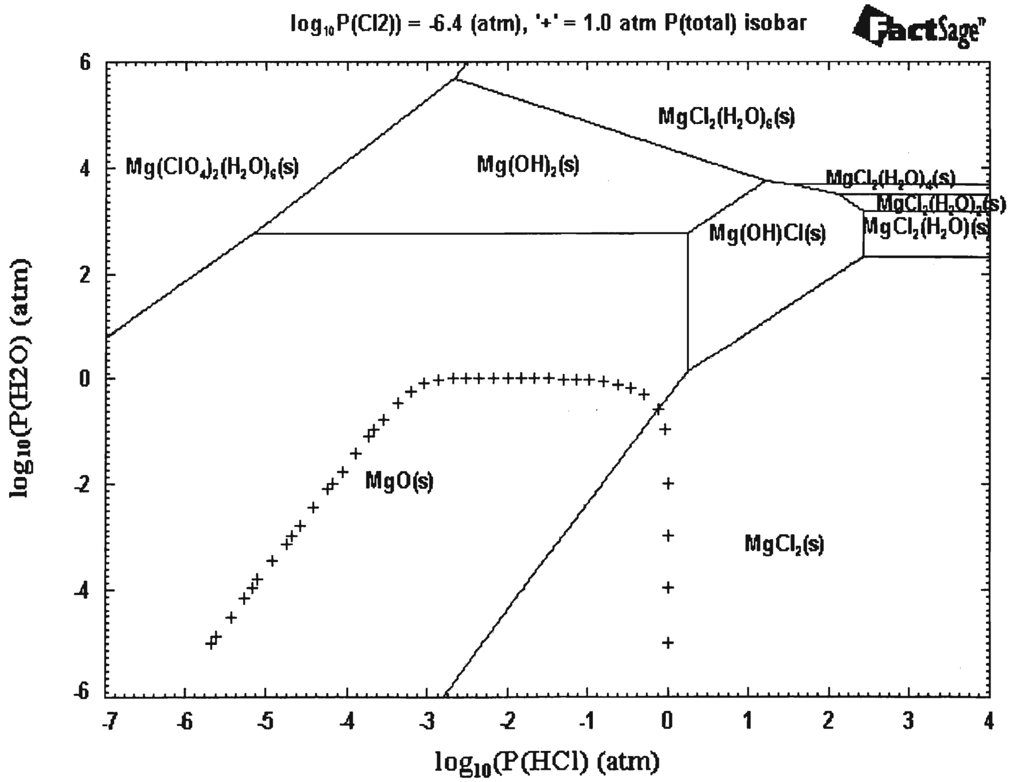

Figure 21: Predominance Diagram of Mg-Cl-O-H System, 873 K $P_{Cl2} = 3.98 \times 10^{-7}$).

- At 473 K, the dehydration of $MgCl_2.4H_2O$ to $MgCl_2.2H_2O$ can proceed according to Reaction 23 without the formation of MgOHCl, if $P_{HCl} = 0.01$ atm or higher.

- At 473 K, the dehydration of $MgCl_2.2H_2O$ to $MgCl_2.H_2O$ according to Reaction 25 is possible only if $P_{HCl} = 0.05$ atm or higher. Dehydration in atmosphere with P_{HCl} less than 0.05 atm results in formation of MgOHCl according to Reaction 27.

- At 473 K, it is possible dehydrate $MgCl_2.H_2O$ to produce $MgCl_2$ according to Reaction 29 only at low P_{H2O} ($P_{H2O} = 0.01$ atm). Otherwise dehydration of $MgCl_2.H_2O$ proceeds to the formation of MgOHCl according to Reaction 31.

- Increasing dehydration temperature shifts the minimum P_{HCl} required for preventing hydrolysis to higher values. For example, to dehydrate $MgCl_2.4H_2O$ to $MgCl_2.2H_2O$ at 673 K, a minimum P_{HCl} of 1 atm is required to prevent formation of MgOHCl.

- At all temperatures, production of $MgCl_2$ without hydrolysis is possible if P_{HCl} approaches 1 atm.

- The hydrolysis products are MgOHCl at low temperature and MgO at higher temperatures.

It is clear that, with careful control of the dehydration gas composition, it is possible to avoid hydrolysis under equilibrium conditions. There are numerous commercial anhydrous $MgCl_2$ production processes that were developed based on this idea.

4.5: Stability of MgOHCl

Moldenhaur[3] found experimentally that when MgOHCl is heated above 527 °C, it decomposed with the formation of HCl[3]. MgOHCl may decompose according to Reaction 33.

$$MgOHCl_{(s)} \leftrightarrow MgO_{(s)} + HCl_{(g)} \tag{33}$$

$$\Delta G^{0}_{(12)}\Big|^{923K}_{298K} = 98581 - 117.63T \left(\frac{J}{mole}\right)\text{[8]} \tag{34}$$

The decomposition temperature of MgOHCl, i.e., the temperature at which the pressure of HCl reaches 1 atmosphere, is calculated from Equation 34 to be 565 °C [1,2,8]. Above this temperature the MgOHCl formed during dehydration will be converted entirely to MgO according to Reaction 33.

4.6: Composition of Hydrolysis Products

Savinkova and Vil'Nyanski[11,15], following Moldenhauer and Kelly's works[3,8], studied the solid phase region of MgO-HCl-H_2O phase diagram. They concluded that the oxide species in this system are either magnesium hydroxychloride compounds or magnesium oxide. They also reported that the product of hydrolysis can be in the form of MgCl(Cl,OH) or solid solutions of Mg(OH)Cl within the lattice of the magnesium chloride depending on the gas composition and the temperature. Such solids, sometimes referred to as 'solid state solutions', are considered to be non-stoichiometric magnesium hydroxychlorides, i.e., compounds of magnesium, oxygen, hydrogen, chlorine and water in the form of, $Mg_x(OH)_yCl_z.nH_2O$, where the values of x, y, z and n are variable. Savinkova and Vil'Nyanski also showed that increasing the temperature increased the MgOHCl content.

In addition, at a specified temperature, the amount of MgOHCl present was found to be directly dependent on the gas composition and independent of the starting material which was either $MgCl_2$ or MgO. Table II presents the MgOHCl content in a solid solution of MgOHCl in $MgCl_2$.

Table II: Solubility of MgOHCl in $MgCl_2$ with Mixtures of HCl and H_2O[11,15].

Temperature (°C)	310	342	350	385	420	450	467	480
MgOHCl content (mole %)	12	15	16	20	25	30	35	40
HCl content (vol.%)	75.4	70.6	69.4	64.4	60.0	56.3	54.2	52.9
H_2O content (vol.%)	24.6	29.4	30.6	35.6	40.0	43.7	45.8	47.1

Reaction 35 presents the equilibrium between magnesium chloride, magnesium hydroxychloride, water vapour and HCl gas.

$$MgCl_{2(ss)} + H_2O_{(g)} \leftrightarrow MgOHCl_{(ss)} + HCl_{(g)} \qquad (35)$$

$$\Delta G^0 = -2170 - 33.9T + \log T - 5.8\times10^{-3}T^2 - 1.03\times10^5 T^{-1} \left(J/_{mole} \right) \quad (36)$$

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Chapter 5: Novel Algorithm for Magnesium Oxides Speciation

5.1: Summary of Invention

The present authors have developed a novel and accurate method to determine the composition (of) and amount(s) of magnesium oxides present in dehydrated magnesium electrolysis process feed or fused salt melts used for commercial magnesium production process electrolytes regardless of nature of the oxide species that are present. The method overcomes the limitations of previous techniques, especially with regard to considering different forms of hydroxychlorides in the sample and other impurities. The present technique is based on any oxygen present in the samples of interest here that is combined with magnesium and / or chlorine and hydrogen, is either in the form of MgO or one of the identified magnesium hydroxychloride species listed in Table III.

Table III: List of Identified Magnesium Hydroxychloride Compounds.

Compounds	Molar Mass (g/mol)	Mass Fraction			Reference
		Mg	O	Cl	
$Mg(OH)Cl$	76.8	0.32	0.21	0.46	(13,17,23,1,2,3)
$Mg_2(OH)_3Cl$	135.1	0.36	0.36	0.26	(1,4,5,6,7)
$Mg_2(OH)Cl_3$	172.0	0.28	0.09	0.62	(1)
$Mg_3(OH)_2Cl_4$	248.7	0.29	0.13	0.57	(1)
$Mg_3(OH)_5Cl$	193.4	0.38	0.41	0.18	(1,5,6)
$Mg_3(OH)_4Cl_2$	211.8	0.34	0.30	0.33	(1,1,4,6)
$Mg_{10}(OH)_{18}Cl_2$	620.0	0.34	0.41	0.10	(1,6)

With the discovery that there exists a fixed molar ratio between Mg, OH and Cl in a particular hydroxychloride species and the solubilities of all magnesium hydroxylchloride species in methanol are negligible, it becomes possible to perform a simple procedure involving standard solid/liquid separation and acid/base titration to determine the composition and amounts of magnesium oxide and hydroxychloride species present in the process feed or electrolyte samples.

The present method is less sensitive to the absorbance of moisture by the sample and is substantially free from error due to the presence of impurities. It can also analyze large sample masses thereby greatly improving analytical precision.

5.2: McGill Magnesium Oxide Speciation Technique

The procedure for the determination of the composition and amounts of magnesium oxides present in a sample, is as follows:

1. Mix the test sample with a sufficient amount of ultra-pure methanol to dissolve all the soluble materials[8,53]. This step is called 'methanol leaching'.
2. Filter the mixture from methanol leaching.
3. Set aside the filtrate and thoroughly wash the filter residue with pure methanol.
4. Dry the residue at 100 °C, a temperature that is not high enough to change the composition of residue or the species present but is sufficient to evaporate all residual methanol and eliminate any oxygen contamination from residual methanol.
5. Divide the residue to two equal weight portions and record the sample weight (M^{BC}).
6. Dissolve one portion of the dried filter residue in 0.1 N HCl (hydrochloric acid).
7. Analyze the solution by titration with sodium hydroxide solution to determine the "Total Acid Consumption Before Decomposition (TAC^{BC})" due to existence of oxides in the residue when it was added to the 0.1 N HCl.
8. Heat another portion of sample to about 700 °C under open atmosphere to convert the magnesium hydroxylchloride in the sample into MgO (magnesium oxide) and record the sample mass after decomposition (M^{AC}). The chosen temperature is sufficient to convert all magnesium containing compounds into MgO[6].
9. Dissolve the decomposition products in the 0.1 N HCl (hydrochloric acid).

10. Analyze the solution by titration with sodium hydroxide solution to determine the Total Acid Consumption After Decomposition (TAC^{AC}).

11. Calculate the number of moles of MgO and the number of moles of hydroxylchloride in the sample using the following equations together with the acid consumption before and after decomposition (A and B) per mole of hydroxychloride given in Table IV for each of the possible form of hydroxychlorides using Eqn 37 and 38.

$$Mole\,MgO = \frac{1}{2}\left(TAC^{BC} - \frac{A}{B-A}\right)\left(TAC^{AC} - TAC^{BC}\right) \qquad (37)$$

$$Mole\,hydroxylchloride = \frac{TAC^{AC} - TAC^{BC}}{B-A} \qquad (38)$$

12. Calculate the mole of hydroxychloride in the sample from the sample mass before and after decomposition using Eqn 39 for each of the possible form of hydroxychlorides, where $MW_{Mgx(OH)yClz}$ and MW_{MgO} are the molecular weight of the hydroxychloride of interest and MgO respectively.

$$Mole\,hydroxylchloride = \frac{M^{BC} - M^{AC}}{MW_{Mgx(OH)yClz} - A\left(MW_{MgO}\right)} \qquad (39)$$

13. Compare the calculated amount of hydroxychloride from Eqn 38 and 39 to identify the form of hydroxychloride in the sample and MgO and hydroxychloride content in the sample, Figure 22.

Table IV: Acid Consumption of Hydroxychlorides before and after Decomposition.

Compound ($Mg_x(OH)_yCl_z$)	Molecular Weight ($MW_{Mgx(OhyClz)}$)	Acid Consumption per mole of Hydroxychloride before Decomposition (A)	Acid Consumption per mole of Hydroxychloride after Decomposition (B)
$Mg(OH)Cl$	76.76	1	2
$Mg_2(OH)_3Cl$	135.06	3	4
$Mg_2(OH)Cl_3$	171.97	1	4
$Mg_3(OH)_2Cl_4$	248.73	2	6
$Mg_3(OH)_5Cl$	193.37	5	6
$Mg_3(OH)_4Cl_2$	211.82	4	6
$Mg_{10}(OH)_{18}Cl_2$	619.96	18	20

Note:

1. Methanol leaching removes the hygroscopic chloride salts from the sample and the residue's subsequent dissolution in the hydrochloric acid eliminates moisture pickup with the result that the sample is stable with respect to contamination with moisture; unlike the other speciation techniques.
2. Ultra-pure methanol with very low water content is used in order to prevent any possible reaction between water and the sample.

The calculation procedure of the proposed speciation technique is illustrated in the following sample calculation. Assuming an electrolyte sample contains 0.2 g of MgO and 0.1 g of hydroxychloride in the form of $Mg_2(OH)_3Cl$, then the mass of residue isolated from the methanol leaching will be 0.3 g. When equal portion of the residue (i.e. 0.15 g) is titrated against hydrochloric acid, the total acid consumption before and after decomposition are 6.073×10^{-3} mole and 6.443×10^{-3} mole, respectively. The mass of sample after decomposition is 0.1298 g. Using the equations provided and the parameters listed in Table IV, the mass of MgO and hydroxychloride is calculated for each possible form of hydroxychloride as shown in Table V.

Table V: Results of Sample Calculation.

Compound	Mole of MgO from Eqn 37	Mole of Hydroxychloride from Eqn 38	Mole of Hydroxychloride from Eqn 39
$Mg(OH)Cl$	2.851E-03	3.702E-04	5.530E-04
$Mg_2(OH)_3Cl$	2.481E-03	3.702E-04	3.702E-04
$Mg_2(OH)Cl_3$	2.975E-03	1.234E-04	2.207E-04
$Mg_3(OH)_2Cl_4$	2.944E-03	9.255E-05	1.577E-04
$Mg_3(OH)_5Cl$	2.111E-03	3.702E-04	2.782E-04
$Mg_3(OH)_4Cl_2$	2.666E-03	1.851E-04	2.217E-04
$Mg_{10}(OH)_{18}Cl_2$	1.370E-03	1.851E-04	9.294E-05

As can be seen, the mole of hydroxychloride in the sample calculated from Eqn 38 and 39 are identical. Therefore, it can be concluded that the form of hydroxychloride in the sample is $Mg_2(OH)_3Cl$ and the mass of MgO and hydroxychloride in the same is 0.3 g and 0.2 g. If the sample content only MgO, the calculation results will be identical for each hydroxychloride species with mass of hydroxychloride equal to zero and calculated mass of MgO equal to the sample mass.

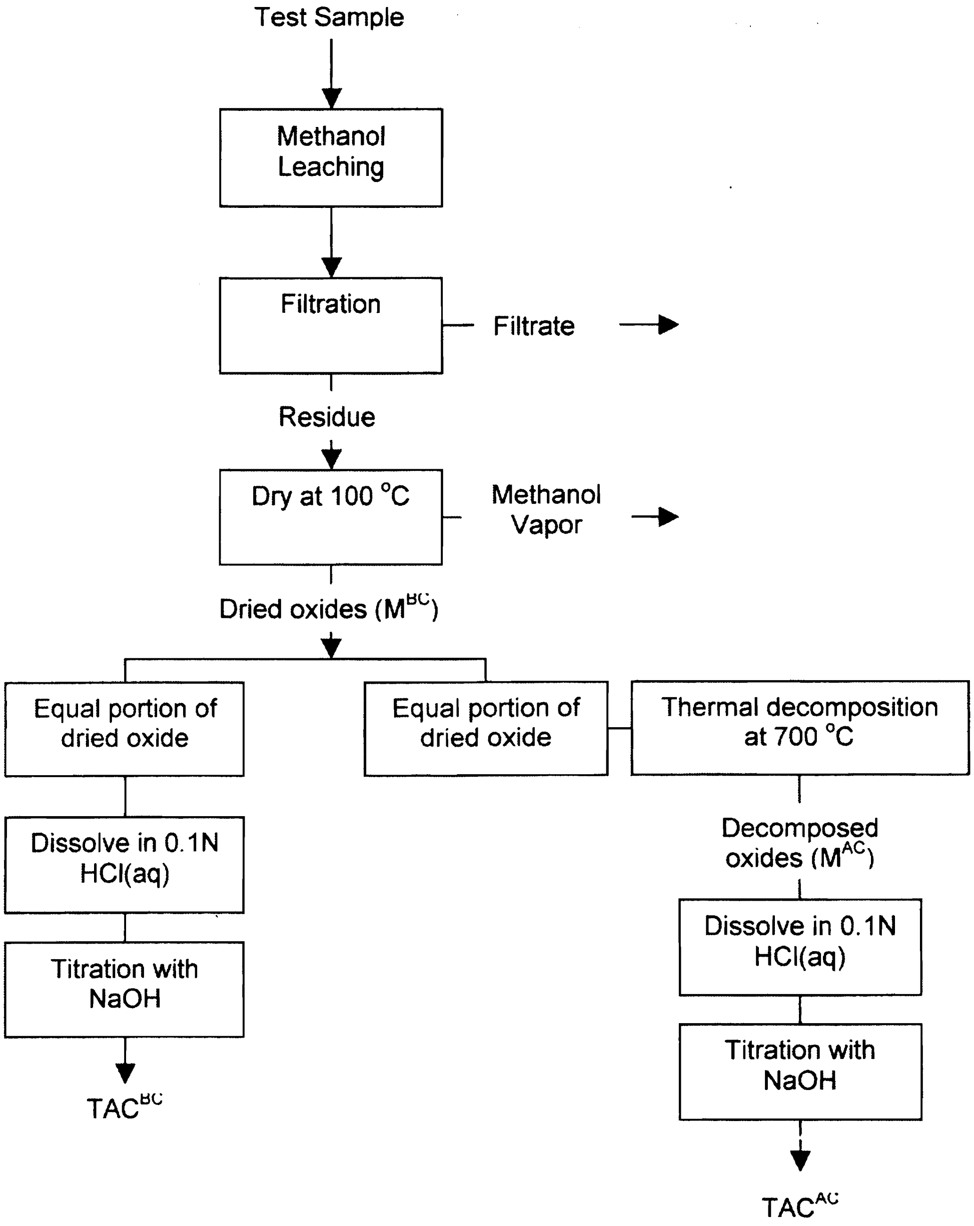

Figure 22: Schematic Representation of the Procedures of the McGill Speciation Technique.

5.3: Introduction and Background of Invention

There are two generic processes for the commercial production of magnesium. One involves thermal reduction of magnesium oxide compounds under vacuum and the other involves the electrolytic reduction of magnesium chloride dissolved in a fused salt. At the present time, the thermal reduction route contributes more than 60 % of the world's magnesium production, although the 'electrolytic route' is more amenable to scale up and reduction in operating costs as well as having less negative impact on the environment per kilogram of produced magnesium. As a result, the latter is likely to be the dominant process for new magnesium production capacity in the future.

A number of variations on the commercial magnesium electrolytic route have been developed in the last 40 years by different ventures, for example, Dead Sea Magnesium[9], Hydro Magnesium[10], Magnola Metallurgie[11], Australian Magnesium Corporation[12], etc. Each variation purifies an aqueous solution containing magnesium chloride to produce a nominally anhydrous magnesium chloride feed for the electrolytic operation. A common challenge in all variations is that the magnesium chloride loaded fused salt (that is) used as the electrolyte must be virtually free of oxygen and/or oxygen containing compounds since any oxygen present will either react with and consume the components of the electrolysis cells and/or it will form stable compounds that interfere with the performance and severely lower productivity of the electrolytic cells.

An analysis of the thermodynamics of the precipitation of magnesium chloride from aqueous solution revealed that the first solid to precipitate under ambient conditions is magnesium chloride hexahydrate ($MgCl_2.6H_2O$). Unless special and expensive precautions are undertaken, the resultant dehydrated product of $MgCl_2.6H_2O$ can contain significant quantities of oxygen-containing compounds, which will enter the fused salt electrolyte and will cause the problems mentioned above.

The oxygen-containing compounds found in the $MgCl_2.6H_2O$ dehydration product are either in the form of MgO or as 'hydroxychlorides'. As the physical and chemical properties of MgO are different for the various forms of hydroxychlorides, different techniques may be required for controlling the MgO and hydroxychlorides content in the electrolyte. For the purpose of developing an effective technique to control as well as monitoring the oxygen-containing compound content in the electrolyte, it is essential to have an oxide speciation technique able to determine the form of hydroxychloride and the content of both MgO and hydroxychloride in the electrolyte or dehydration product sample. In practice, the amount and composition of oxide species formed as a result of dewatering of the magnesium chloride aqueous solutions is believed to be controlled by a number of parameters, such as the kinetics of dehydration, temperature and HCl content of the dewatering atmosphere. A reliable speciation technique has the ability to monitor the form and amount of oxide produced during the dehydration process and is essential for further process development in production of anhydrous $MgCl_2$ feed.

An accurate oxide speciation technique for electrolytic magnesium production has eluded the industry to date due to the very powerful hydroscopic nature of magnesium chloride and the seemingly random complexity of the resulting hydrolysis products. The techniques developed to date have also suffered from the inability to assay industrial electrolytes that contain various impurities that can severely lower the accuracy of the technique.

A number of chemical analysis techniques that determine the amount and composition of the oxygen containing compounds found in the feed to the electrolysis operation or in the fused salt electrolytes have been developed previously and are described below. However, all have been unsuccessful for various reasons. The remainder of this report first describes the possible oxides that can be present in magnesium electrolysis feeds and then outlines the existing methods of oxide speciation. The effects of impurities likely to be found in industrial samples are then presented and the report is finished with a validation of the current technique and sample calculations.

5.4: Magnesium Compounds Containing Oxygen Found in Commercial Magnesium Production

Savinkova and Vil'Nyanski[13], following Moldenhauer and Kelly's works[14,15], studied the solid phase region of MgO-HCl-H_2O phase diagram. They concluded that the oxide species in this system are either magnesium hydroxychloride compounds or magnesium oxide. They also suggested that magnesium hydroxychloride compounds can be described as a solid solution of $Mg(OH)Cl$ within the lattice of magnesium chloride. Such 'solid state solutions' are considered to be a compound of magnesium, oxygen, hydrogen, chlorine and water of the form, $Mg_x(OH)_yCl_z.nH_2O$, where the values of x, y, z and n are variable and depend on the conditions during formation.

Vil'Nyanski, Bichikhina and Orekhova[16,17,18] also reported the existence of $Mg_x(OH)_yCl_z$ without crystalline water in hydrolyzed carnallite melts ($NaCl\text{-}KCl\text{-}MgCl_2$). Kochergin[19] and Boghosians[20] reported oxychloride ($Mg_{m+n}O_{2m}Cl_n$) complexes were produced by MgO dissolution in $MgCl_2$ and $MgCl_2\text{-}MgF_2$ melts:

$$MgO_{(l)} + MgCl_{2(l)} = Mg_2OCl_{2(l)} \qquad (40)$$

Inyushkina[21], and more recently Mediass and Ostvold[22], studied the solubility of MgO in alkali metal chloride melts. They found that the solubility of MgO in molten salt systems for electrolytic magnesium production is negligible, of the order of 10^{-5} wt.%. On the other hand, Savinkova et al.[23,24] found that the solubility of Mg(OH)Cl in these same molten salts was a function of temperature, magnesium chloride concentration and P_{HCl} and can reach up to 8 wt.%.

The thermodynamic conditions for formation of solid Mg(OH)Cl and its decomposition to MgO, have been studied by Strelets[25] and later by Kipouros and Sadoway[26]. These authors have stated that at temperatures higher than 565 °C and in the absence of HCl gas, pure solid Mg(OH)Cl decomposes to MgO. Ivanov and Zuev[27] also studied the hydrolysis of magnesium chloride in electrolyte and reported similar conditions for decomposition of dissolved Mg(OH)Cl to MgO[28,29].

5.5: Other Compounds Found in Commercial Magnesium Production

Donkish[30], Mizhzhavlev[31] and Toshid et al.[32] found that the composition of impurities in industrial electrolytes depends on the proceeding feed preparation and refining processes. The impurities are mainly in the form of metal chloride salts and metal particles but also included, silica, borates, sulfates and magnesium oxides.

Strelets[25] and Frantasev et al.[33,34] studied the behavior of metal chloride impurities in the magnesium electrolysis process and concluded that ferric iron in the electrolyte may be electrolytically reduced at the cathode and become re-oxidized to the ferric state at the anode. Furthermore, and more importantly for the present instance since it affects the assay technique, ferric and ferrous iron may react with magnesium to produce metallic iron as follows:

$$2\,FeCl_3 + 3\,Mg = 3MgCl_2 + 2Fe \qquad (41)$$

$$FeCl_2 + Mg = MgCl_2 + Fe \qquad (42)$$

The metal produced contaminates the electrolyte. Manganese, titanium, nickel, and chromium are reported to have similar behavior[35,36,37].

Muzhzhavlev[38] and Frantasev[39] reported that SiO_2 reacts with magnesium to form insoluble magnesium silicide and magnesium oxide according to following reaction:

$$SiO_2 + 4Mg = Mg_2Si + 2MgO \qquad (43)$$

Frantasev[40] and Sabirov et al.[41] summarized the interaction of magnesium with the likely impurities as follows:

Table VI: Interaction of Magnesium with Impurities.

Compounds of	Reaction with Mg
Cr	$2Mg + 2CrCl_3 = 3MgCl_2 + 2Cr$ $Mg + CrCl_2 = MgCl_2 + Cr$ $3Mg + Cr_2O_3 = 3MgO + 2Cr$
Mn	$Mg + MnCl_2 = MgCl_2 + Mn$ $Mg + MnO = MgO + Mn$
Fe	$3Mg + 2FeCl_3 = 3MgCl_2 + 2Fe$ $Mg + FeCl_3 = MgCl_2 + Fe$ $2Mg + Fe_2O_3 = 3MgO + 2Fe$
Al	$3Mg+2AlCl_3 = 3MgCl_2+2Al$ $3Mg + Al_2O_3 = 3MgO + 2Al$
Ni	$Mg + NiCl_2 = MgCl_2 + Ni$ $Mg + NiO = MgO + Ni$
Si	$2Mg + SiO_2 = 2MgO + Si$ $2Mg + SiCl_4 = 2MgCl_2 + Si$

As can be seen, iron, manganese, nickel, aluminum, chromium and silicon can exist as chlorides or reduced metallic particles possibly suspended in industrial electrolytes and a reliable analytical technique needs to accommodate the effects of such impurities if present.

Furthermore, by and large industrial magnesium electrolytes are mixtures of $MgCl_2$, NaCl, $CaCl_2$ and KCl. However, fluorides are also added in the form of MgF_2, CaF_2 and NaF compounds to enhance the electrode reactions. These fluorides undergo an exchange reaction with magnesium chloride in the electrolyte to form magnesium fluoride with the result that any fluorine in the electrolyte will be present as MgF_2. The Standard Gibbs Energies for this exchange reaction for the main species likely to be present are:

$$MgCl_2 + CaF_2 = MgF_2 + CaCl_2 \quad \Delta G^{o}|_{600^{o}C} = -\ 53.8\ \text{kJ/mol} \qquad (44)$$

$$MgCl_2 + 2NaF = MgF_2 + 2\ NaCl \quad \Delta G^{o}|_{600^{o}C} = -\ 162\ \text{kJ/mol} \qquad (45)$$

As long as $(a_{MgCl2}/a_{CaCl2})|_{electrolyte} > 6.0 \times 10^{-4}$ and $(a_{MgCl2}/(a_{NaCl2})^{2}|_{electrolyte} > 2.0 \times 10^{-10}$, the reactions above will go to the right. A similar exchange would be observed for CaO to $CaCl_2$ as per the thermodynamics of the reaction:

$$CaO + MgCl_2 = CaCl_2 + MgO \quad \Delta G^{o}|_{600^{o}C} = -\ 122\ \text{kJ/mol} \qquad (46)$$

As long as $(a_{MgCl2}/a_{CaCl2})|_{electrolyte} > 8.3 \times 10^{-8}$, the reaction above will go to the right.

5.6: Previous Techniques for the Analytical Determination of the Products of $MgCl_2$ Hydrolysis

5.6.1: Volumetric Determination of Hydrogen

Vil'Nyanski, et al.[42] developed a method, known as the magnesium method, in which the volume of hydrogen produced according to the following reactions when a sample of carnallite melt was contacted with incandescent magnesium was measured.

$$2MgOHCl_{(s)} + Mg_{(s)} = 2MgO_{(s)} + MgCl_{2(s)} + H_{2(g)} \qquad (47)$$

$$MgOHCl_{(s)} = MgO_{(s)} + HCl_{(g)} \qquad (48)$$

$$2HCl_{(g)} + Mg_{(s)} = 2MgCl_2 + H_{2(g)} \qquad (49)$$

The measurement procedure starts with saturation of the magnesium with hydrogen, since the solubility of hydrogen in magnesium is high. Data from Bakke et al.[43] indicate that the solubility of hydrogen in magnesium varies between 25 to 30 cm^3(NTP) / 100 g Mg. After heating the saturated magnesium to 600 °C, a molten carnallite sample is poured into the reaction tube containing the magnesium and the volume of gas evolved is read and converted to hydrogen content in the carnallite, Figure 23. The analysis itself, without considering the saturation period that takes roughly 2 and half hours, takes only about 3 minutes. A relative error of 4 % was obtained when replicates of dehydrated carnallite samples were analyzed. The problems with this analytical method are its overestimation of the hydrogen content due to moisture pick-up by the extremely hygroscopic samples since magnesium reacts with moisture from the sample according to the following reaction:

$$H_2O_{(g)} + Mg_{(s)} = MgO_{(s)} + H_{2(g)} \tag{50}$$

Furthermore, this method cannot distinguish between the various forms of magnesium hydroxychloride that might be present since it is assumed that the only hydroxychloride in the sample is in the form of MgOHCl.

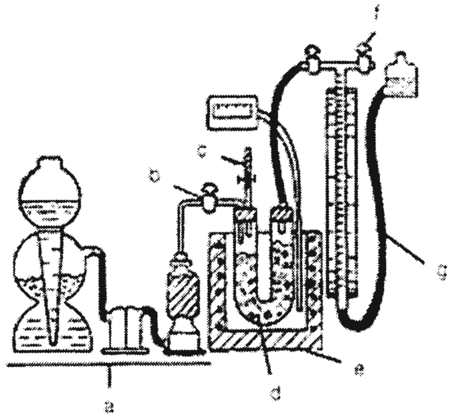

Figure 23: Apparatus for the Determination of Hydrogen in Dehydrated Carnallite Samples.

a) Hydrogen Supply, b) Inlet Valve, c) Test Tube,
d) Reaction Tube with Mg Shavings, e) Furnace,
f) Purge Valve, g) Burette

Vil'Nyanski et al.[44] developed another volumetric method of determining the hydrogen content of dehydrated carnallite. In this method, aluminum is used instead of magnesium. The solubility of hydrogen in solid aluminum is about 0.25 cm^3 (NTP) / 100 g Al which is much lower than in solid magnesium. Therefore, it is possible to reduce the saturation period from 2.5 hours to 40 minutes. However, the uncertainty on the form of hydroxychloride is not addressed.

5.6.2: Alkalimetric Speciation

Savinkova et al.[45] proposed a method to overcome the problem of moisture contamination in the volumetric determination of hydrogen. The method was developed on the basis of the difference in the rates of titration of the products of dissolution of a carnallite sample in water. When a carnallite sample containing MgOHCl is dissolved in water, it forms $Mg(OH)_2$ according to the reaction:

$$2MgOHCl_{(S)} = Mg(OH)_{2(S)} + MgCl_{2(aq)} \qquad (51)$$

As argued by the authors, MgOHCl is a dissolved species in carnallite and its dissolution in water leads to the precipitation of very fine $Mg(OH)_2$ particles that react rapidly with the titration acid. The MgO in the carnallite also reacts with water as follows:

$$MgO_{(s)} + H_2O_{(l)} = Mg(OH)_{2(aq)} \qquad (52)$$

Fruhwirth et al.[46] studied the dissolution and hydration kinetics of MgO in water. They found that MgO slowly hydrolyzes in water and the rate limiting step was not the reaction with $Mg(OH)_2$, but rather the hydrolysis of MgO.

Thus when the carnallite containing MgO and MgOHCl is dissolved in water and titrated with an acid, there are two stages of acid consumption. The first stage is associated with the titration of $Mg(OH)_2$ from the dissociation of MgOHCl. The second stage consists of slow titration due to the slow reaction of MgO with the acid. The MgO and $Mg(OH)_2$ particles are assumed to react with the acid following a shrinking core model without a reaction product being deposited at the surface of the particle.

In practice, the alkalimetric speciation procedure consists first of a total alkalinity measurement of the sample, expressed as MgO equivalent (MgO_{eq}). Following this, a mass of sample equivalent to 0.1 g of MgO_{eq} is dissolved in water. The sample is titrated with 0.1N H_2SO_4 in the presence of methyl red indicator. The amount of acid added to the sample is recorded as a function of the time and converted to an equivalent content of reacted magnesium oxide. The amount of MgO_{eq} left unreacted is computed and $(MgO_{eq})^{1/3}$ is plotted as a function of time.

Three distinct zones are observed in the '*typical*' titration curves, Figure 24. The initial slope corresponds to the titration of $Mg(OH)_2$ from MgOHCl. The second part of the curve is attributed to the titration of $Mg(OH)_2$ from 'poly-disperse particles of MgO' and the last part of the curve represents the slow hydrolysis and reaction of MgO.

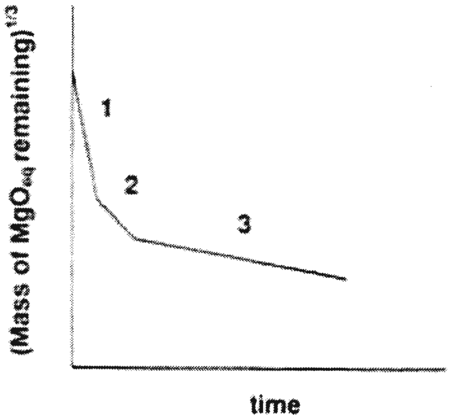

Figure 24: Schematic Alkalimetric Speciation Curve.

Using the titration curve so obtained, the content of MgO in the sample is obtained by extrapolating the second segment of the curve to the vertical axis of the graph. Savinkova[45] checked the validity of the method against the magnesium method and reported the error to be below 3 % for MgO and below 15 % for MgOHCl.

Laroche et al.[47] improved the alkalimetric speciation method by monitoring the titration pH with an indicator electrode and using an automatic titrator. They reported difficulties in interpreting titration curves for samples with low Mg(OH)Cl content that resulted in significant error in the measurements of low Mg(OH)Cl samples. They concluded that this method was at best a semi-quantitative.

5.6.3: Carbothermal Reduction

Vinstad et al.[48] used a carbothermal reduction technique to determine the MgO and MgOHCl contents in hydrolyzed $MgCl_2$ and $MgCl_2$-NaCl melts. They assumed that the only hydrolysis products were MgO and MgOHCl such that the total oxygen content and the base equivalent oxygen content were accounted for by MgO and MgOHCl as follows,

$$n_o^{tot} = n_{MgO} + n_{MgOHCl} \tag{53}$$

$$n_o^{bas} = n_{MgO} + \frac{1}{2} n_{MgOHCl} \qquad (54)$$

By solving these two equations simultaneously, the MgO and MgOHCl contents of the sample were obtained. The total oxygen content of the sample was determined using a modified LECO TC-436 oxygen and nitrogen analyzer. The analysis began with the fusion of a sample held in a tin capsule in a graphite crucible at about 2200 °C. The oxygen in the sample reacted with the graphite from the crucible to form CO. The CO was oxidized to CO_2 in a CuO tower. The amount of CO_2 formed was determined by infrared absorption spectrometry and the base equivalent oxygen content was determined by iodometric titration.

Since this method measures all the oxygen present in the sample, it is sensitive to moisture pick-up as water adsorbed by the sample reacts with the graphite to form CO or reacts with $MgCl_2$ to form MgO or MgOHCl. Consequently, it was not possible to distinguish between contributions from absorbed water and from oxides already present in the sample. The authors took the following precautions in order to minimize water absorption:

- Samples were kept and handled in a glove box with low water content.
- The equipment used for sample preparation was heated to 150 °C.
- Samples were transferred in the glove box while hot.
- Samples with weight of only 20 mg were analyzed in order to minimize the surface of the sample.

It is important to note the use of very small samples. Such small masses considerably degrade the precision of this method of measurement. Further, the assumption that the oxides present in the electrolyte samples were only MgO and MgOHCl, is another limitation of this technique.

5.6.4: Analytical Oxide Speciation Technique

Hagg[49] described an analytical method developed for determination of magnesium chloride hydro-chlorination products in samples containing MgO, MgOHCl and $MgCl_2$. In his method, weighed samples were dissolved in a minimum amount of nitric acid followed by Cl^- measurement using Mohr's titration with 0.1M silver nitrate ($AgNO_3$) with sodium chromate ($NaCrO_4$) as the indicator. The OH^- and O^{-2} content of sample were determined by back titration of the excess acid used in the dissolution process. Sodium hydroxide (NaOH) was used for titration with phenolpthalein as the indicator. Mg^{+2} was determined by complexometric titration of the solution with ethylenediamine tetra-acetic acid (EDTA) using Erichrome black T as the indicator. By ignoring the presence of H_2O in the test samples, the masses of the MgO, $MgCl_2$ and MgOHCl compounds in the sample, W_{MgO}, W_{MgCl_2}, W_{MgOHCl}, respectively, were calculated by solution of the following set of simultaneous equations where X represents the mass fraction of the species and W represents the mass of species indicated:

$$W_{MgO} + W_{MgOHCl} + W_{MgCl_2} = \text{Weight of Sample} \tag{55}$$

$$X_{O,MgO}\, W_{MgO} + X_{O,MgOHCl}\, W_{MgOHCl} = \text{Total Oxygen} \tag{56}$$

$$X_{Mg,MgO}\, W_{MgO} + X_{Mg,MgOHCl}\, W_{MgOHCl} = \text{Total Magnesium} \tag{57}$$

$$X_{Cl,MgCl_2}\, W_{MgCl_2} + X_{Cl,MgOHCl}\, W_{MgOHCl} = \text{Total Chlorine} \tag{58}$$

This method of measurement is only suitable for analyzing magnesium electrolysis feed and hydrolysis products (of magnesium chloride) and not for electrolyte oxide speciation since other chlorine bearing compounds are present in the electrolyte. Ignoring the existence of non-stoichiometric hydroxychlorides is also another deficiency of this method.

5.6.5: Analytical Oxide Speciation Technique Using Methanol Leaching

Xu et al.[50] developed an analytical method for determination of magnesium electrolyte components. Pure methyl alcohol was used as a selective solvent to separate magnesium, calcium and sodium chlorides from the magnesium and calcium oxides in the electrolyte. After dissolving samples in the methanol, the magnesium and calcium contents in the residue were measured with EDTA compleximetric titration. They ignored the existence of any soluble hydroxychlorides in the electrolyte, which has made their method a semi-quantitative speciation technique with limited reliability.

5.7: Effect of Impurities on Existing Oxide Speciation Measurements

The techniques above have mostly been used for analyzing laboratory-made samples that have been prepared from high-purity chemicals. In general they have not been used for the analysis and speciation of industrial samples that are usually contaminated with impurities such as Fe, Ni, B, Si, Al, Mn, Ti, Cr, C, F^- and SO_4^{2-}. The presence of these impurities interferes with the titration procedures used in alkalimetric and carbothermal methods, affects the total oxygen determination in the carbothermal speciation and in the case of the fluorine, introduces significant error in the magnesium content measurement as required for the Analytical Oxide Speciation Technique of Xu.

5.7.1: Effects of Impurities in the Present Magnesium Oxide Speciation Technique

As mentioned, industrial samples often contain impurities that can be present in the form of chlorides that are readily dissolved and hence removed from the residue during methanol leaching with the result that they do not interfere in the analysis of the residue. Table VII lists the solubilities of various chlorides likely to be found in industrial magnesium electrolyte samples in methanol.

Table VII: Solubility of Metal Chloride Compounds in Methanol at 25 °C.

Compound	Solubility (wt.%)
$CaCl_2$	25.2
$CuCl_2$	36.5
$FeCl_3$	61.7
KCl	0.5
$MgCl_2$	14.3
$MnCl_3$	6.5
NaCl	1.39
$NiCl_2$	9.13

The literature also shows that the solubility of magnesium oxide in methanol is vanishingly small, 1.46×10^{-4} g/100 ml[50]. The solubility of the hydroxychlorides is reported to be negligible[52] and recent results from the current authors indicate that solubility of MgOHCl in methanol is 12.64×10^{-4}g/100 ml.[53] Such selectivity means that the methanol leaching technique is a satisfactory method to isolate the desired constituents of the sample for further analysis.

As mentioned, fluorine in the sample reports as MgF_2 as evidenced by the EDX and XRD spectra identifying an MgF_2 particle in the residue from methanol leaching of industrial electrolyte shown in Figure 25 and Figure 26, respectively. However, it should be noted that dissolution of MgF_2 in the acid does not affect the sample total acid consumption as evidenced by simulation of dissolution of typical impure industrial electrolyte methanol leached residue in the dilute hydrochloric and nitric acid solutions with Fact-Sage and OLI software[54,55]. These simulations revealed that hydrofluoric acid produced by dissolution of the MgF_2, react with metallic impurities, alumina and silica in the sample and cause less than 4 to 5 % error in total acid consumption measurement.

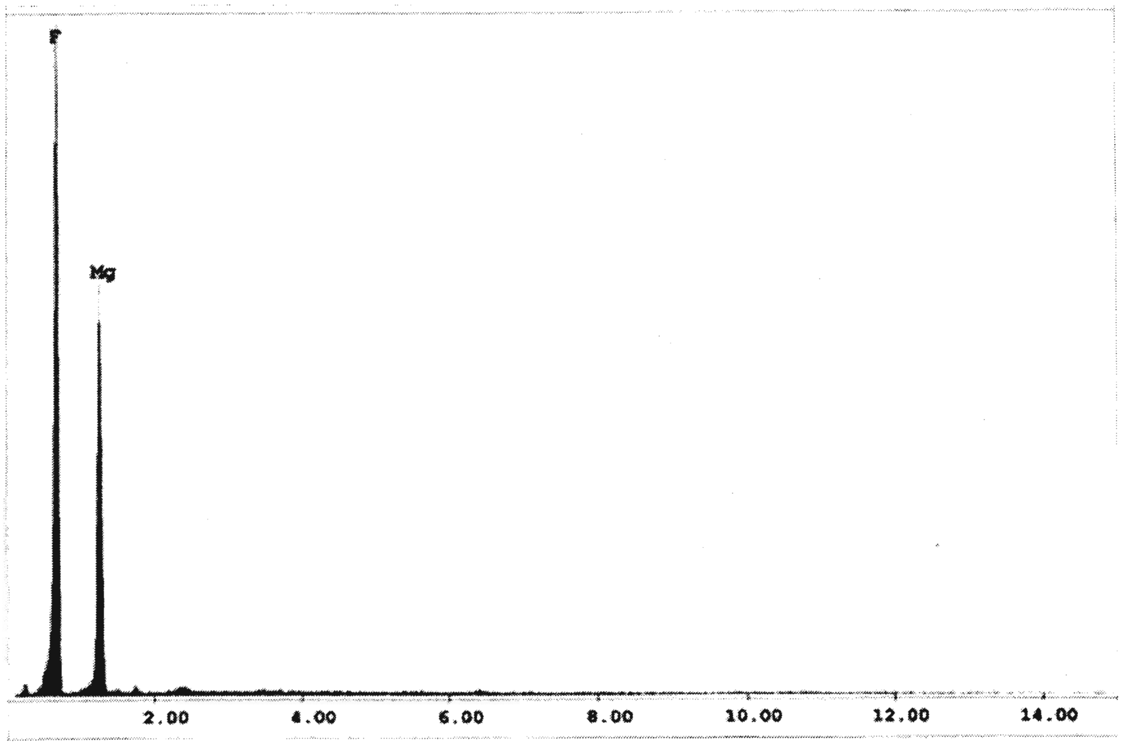

Figure 25: EDX Spectra of MgF_2 Particle In Methanol Leaching Residue.

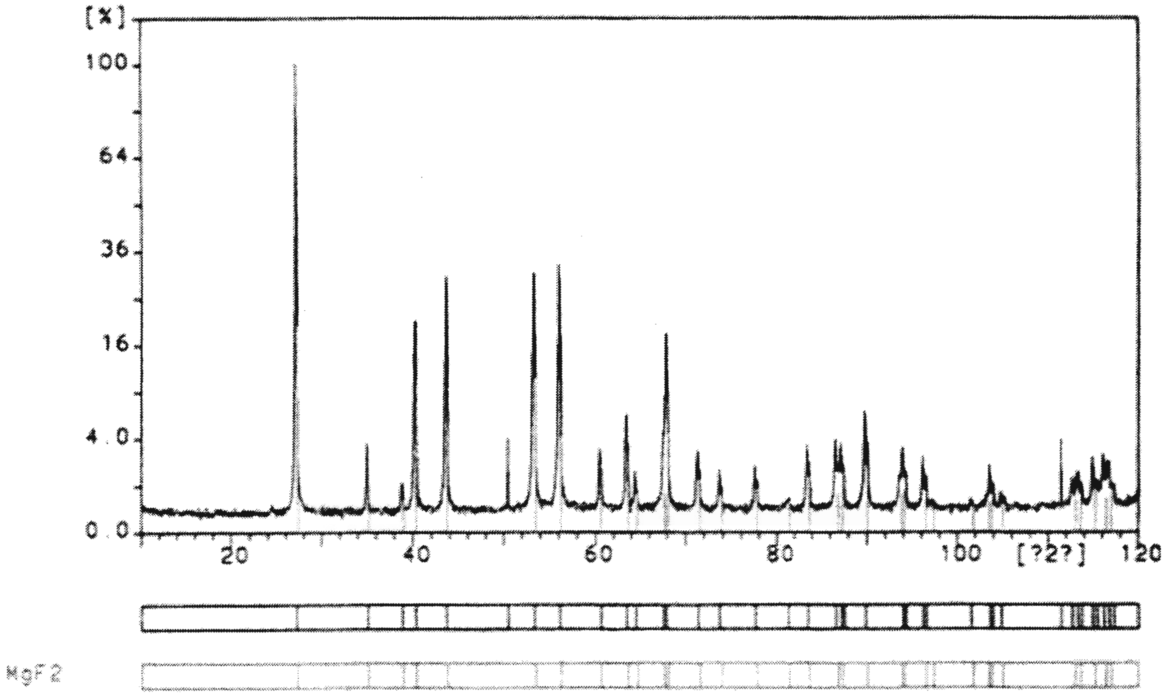

Figure 26: XRD Spectra of Industrial Electrolyte Methanol Leaching Residue.

5.8: Validation of the McGill Speciation Technique

Mg(OH)Cl reference sample was prepared from controlled dehydration of $MgCl_2.6H_2O$. A 0.1 g of sample was prepared with equal amount of Mg(OH)Cl and MgO. The novel speciation technique was applied to these samples for the purpose of validation of the proposed technique. The titration results are summarized in Table VIII and Table IX. It should be noted that accuracy of measurements was estimated on the detection limitation of analytical method used.

Table VIII: Results of Validation Titrations.

	Before Decomposition	After Decomposition
Sample Mass	0.100 g	0.074 g
Total Acid Consumption	3.424E-3 mole	4.074E-3 mole

Table IX: Calculation Results from the Validation Titrations.

Compound	Mole of MgO from Eqn 37	Mole of Hydroxychloride from Eqn 38	Mole of Hydroxychloride from Eqn 39	% Difference between Calculation Results of Eqn 38 and Eqn 39
$Mg(OH)Cl$	1.387E-03	6.499E-04	7.132E-04	9.7 %
$Mg_2(OH)_3Cl$	7.372E-04	6.499E-04	4.775E-04	-26.5 %
$Mg_2(OH)Cl_3$	1.604E-03	2.166E-04	2.846E-04	31.4 %
$Mg_3(OH)_2Cl_4$	1.550E-03	1.625E-04	2.034E-04	25.2 %
$Mg_3(OH)_5Cl$	8.730E-05	6.499E-04	3.589E-04	-44.8 %
$Mg_3(OH)_4Cl_2$	1.062E-03	3.250E-04	2.860E-04	-12.0 %
$Mg_{10}(OH)_{18}Cl_2$	-1.213E-03	3.250E-04	1.199E-04	-63.1 %

As can be seen in Table IX, the difference between the mole of hydroxylchloride calculated from Eqn 38 and Eqn 39 is smallest for $Mg(OH)Cl$. Therefore, it can be concluded that the hydroxylchloride species in the sample is $Mg(OH)Cl$. The calculated mass of MgO and $Mg(OH)Cl$ in the sample using Eqn 37 and Eqn 38 is 0.0599 g and 0.0499 g respectively. It is known that the purity of the $Mg(OH)Cl$ reference sample used in the preparation of the test sample is about 93 % with MgO as the major impurity. When this factor is taken into consideration, the actual mass of MgO and $Mg(OH)Cl$ in the test sample are 0.0535 g and 0.0465 g respectively. The percentage difference between the calculated and actual mass of MgO and $Mg(OH)Cl$ are 4.5 % and 7.3 % respectively.

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Chapter 6: Experimental Procedures

6.1: Scope of Chapter

The experimental techniques used to obtain the results and conclusions presented in this thesis are described in this chapter along with the apparatus and materials used.

6.2: Experimental

The experimental apparatus was consisted of three main components. These components were a tube furnace, a glove box and the process gas handling and purification system, all shown in Figure 27.

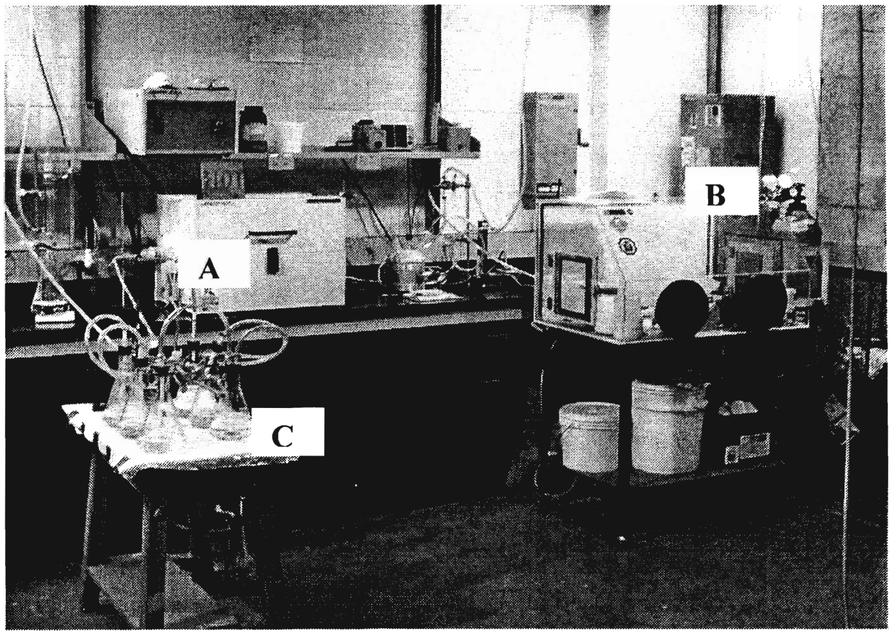

Figure 27: Project Setup.

A: Tube Furnace B: Glove box C: Off-gas purification system.

The amount and composition of the products formed during the dehydration of magnesium chloride hydrates was controlled by the temperature of dehydration, the heating rate and the dehydration and hydrolysis atmosphere. To study the dehydration under specific conditions, a furnace installation was used for all the testing. In this installation the programmable tube furnace was equipped with a quartz process tube to contain the hot stream of HCl and the H_2O released during the dehydration. This assembly was modified as required to obtain the data sought.

Magnesium chloride hydrates and their dehydration products are extremely hydroscopic. Therefore testing with these materials requires special precautions to minimize the risk of water absorption and the resultant change in the composition and amount of reaction products. In this study, sample preparation and processing of materials sensitive to moisture absorbance were performed inside a Terra Universal Series 100 dry glove box[1]. This Polymer Glove Box provides a clean, low-humidity environment for critical processing operations.

The glove box used was equipped with extra dry nitrogen (99.99 %, Matheson) purging system and a relative humidity monitoring device (Omega HR31)[2]. The Dual Purge™ System delivers a variable nitrogen purge into the glove box. During normal operation, it provides a continuous low-flow purge to maintain a positive pressure that blocks out contaminants. In the event of a sudden pressure drop, it activates a high-flow purge to block out contaminants and to quickly purge any moisture or contaminants that do enter the chamber.

A molecular sieve was also used to further purify the purging gas and moisture traps were placed in different locations inside the chamber. The glove box used was equipped with a fast material import sliding gate and all test samples were transferred to the glove box before they cooled completely.

In the high temperature tests, a hot gas stream containing HCl and H_2O was released during dehydration of magnesium chloride hydrates. To protect the furnace itself and its accessories and to respect laboratory health and safety regulations, process off gases were neutralized by bubbling in a series of flat bottom flasks containing NaOH solutions.

6.3: Test Procedure

Chemical grade (99.9 %) bischofite ($MgCl_2.6H_2O$) from Sigma-Aldrich was used. Samples were precisely weighed with a Mettler Toledo B303-S balance (± 0.001 g), and placed in dried and preheated Coors® high alumina combustion boats[3]. The samples were then placed into a 4 cm ID quartz process tube made by Chemglass Inc, with the charging end open to the atmosphere[4]. Dehydration was studied at 200 °C, 300 °C, 400 °C, 500 °C and 600 °C. The programmable furnace from Lindberg Blue, model M1200 Split Hinge, was programmed to heat to these temperatures with heating rates ranging from 1 to approximately 1000 °C/min[5].

Process gas from the furnace was conducted by the mean of quartz tubing to the off gas purification unit. There, off gas contaminated with HCl passed through several flat bottom flasks filled with NaOH solution in water. The purified gas was then conducted to the central ducting system of laboratory. At the end of each test, samples were removed from the furnace and quickly transferred to glove box, with little cooling, where the sample masses were precisely measured. The samples were then leached in ultra pure, dry, methanol (99.995 %, Sigma Aldrich) to dissolve the magnesium chloride and magnesium chloride hydrates and separate them from insoluble oxides[†]. The oxides isolated by methanol leaching were then dried in a Fischer 282A vacuum oven at about 100 °C[6]. This temperature was high enough to evaporate the methanol but not sufficient to change the composition of the oxides. Thereafter, the mass of the oxide were measured and samples analyzed with the McGill Speciation Technique and other standard analytical methods such as X-Ray Diffractometry (XRD), Thermal Gravimetric Analysis (TGA), Acid-Base titration, Atomic Absorption (AA) and Ion Chromatography (IC)[7]. The wastes, e.g., methanol loaded with magnesium chloride, were stored in the proper waste containers and processed through the McGill Hazardous Waste Treatment Facility.

6.4: McGill Speciation Technique

McGill speciation technique has been presented in detail in Chapter 5 of this thesis.

[†] The water content of methanol before and after dissolution procedue was not measured.

6.5: Standard Analytical Techniques

6.5.1: Thermal Gravimetric Analysis (TGA)

To analyze the sequence of thermally induced reactions and to identify the conversion temperatures, Thermal Gravimetric Analysis of samples was performed with a Cahn Thermo 700 TGA machine[8]. Prior to each test, machine was calibrated by measuring the weight of two calibration weights and the internal balance was tarred according to the manufacturer's instructions. A sample of 0.1 to 0.2 g of the test material was charged to a high alumina crucible and then placed in the furnace that was purged with ultra pure, dry helium. Helium was purified using an Air Products OMI-2 gas purifier and a NanoChem resin used as the moisture absorbent[9]. Samples were heated to 600 °C at a heating rate of 10 K/min, kept at 600 °C for 30 min and then allowed to cool by natural convection.

6.5.2: X-Ray Diffractometry

X-ray diffraction analysis was used for qualitative analysis of different compounds in test samples and to follow the chemical transformation of a specific material as a function of temperature and time of holding. XRD was performed with a Philips PW 1710 diffractometer using a copper tube X-ray source and operating at 40 kV and 40 mA. Samples were ground using an agate mortar and spread into aluminum sample holders fro mounting in the goniometer. The diffraction pattern of unknown material was compared with the PC-APD (PW-1877) Analytical Powder Diffraction Software[10] and Hanawalt Reference Database[10] in order to identify the chemical compound.

6.5.3: Fourier Transformation Infrared Spectrometry (FT-IR)

IR samples were prepared using a standard mulling technique[11]. IR spectra acquisition was performed with a Bruker IFS66 spectrometer[12]. The system comprised a DTGS detector equipped with a KBr window[12]. This type of window covered mid-range infrared wavelengths from 4000 to 400 cm^{-1}. Data treatment was performed using Optic User Software, OPUS, V 2.2 software[13].

The mulling technique is an easy and fast technique that has been used in analysis of inorganic materials. The technique consists of mixing the powdered material with a few drops of oil, namely Fluorolube®, as a mulling-agent[14]. The mixture was ground in an agate mortar to disperse the solid in the oil. The mixture was then spread on a KBr window and a second KBr window was squeezed against the first to form a thin film of material to be examined. Fluorolube® is a fluorinated hydrocarbon solvent that is ideal for preparation of samples to be run from 4000 to 1360 cm^{-1}, where it is non-absorbing, except at 2321.9 cm^{-1}. As a result, Fluorolube did not interfere with the hydroxyl group absorption peak at around 3800 cm^{-1}. The absorption spectrum of Fluorolube is presented in, Figure 28.

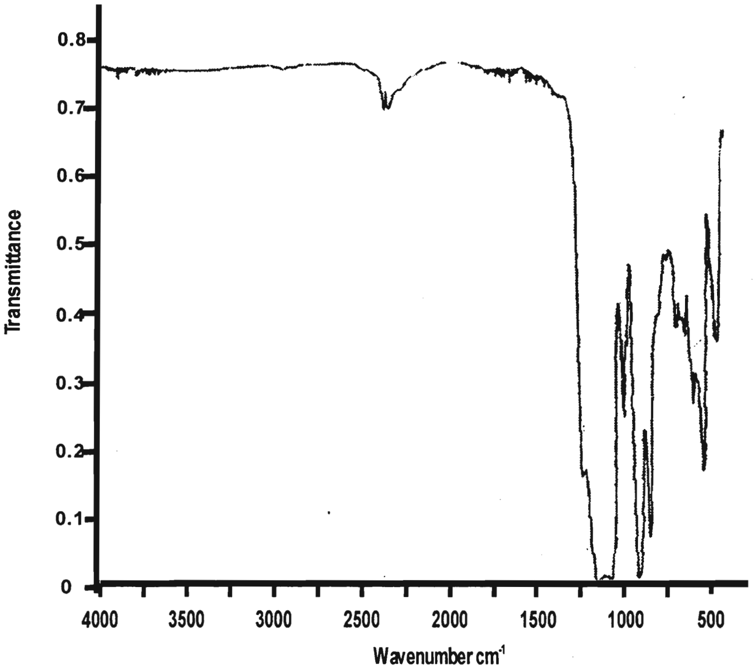

Figure 28: IR Absorption Spectrum of Fluorolube.

6.5.4: Determination of Total Alkalinity

In titrimetry, materials or group of materials are quantified by measuring the volume of a reagent solution with known concentration of a substance, the titrimteric solution which is required for a defined, complete chemical conversion with the material that are to be analyzed.

The total alkalinity of samples was determined using an automatic titration system. Approximately 0.1 g of sample was precisely weighed using a Mettler Toledo B303-S analytical balance. The sample was then dissolved in a specified amount of a 0.1N HCl solution. The prepared solution was vigorously stirred to ensure complete digestion of the solid into the aqueous phase. Titrations were carried out using a TitroLine automatic titrator. A 0.1N NaOH solution was used as the titrant and each analysis campaign started with the titration of the titrant and then the test samples.

6.5.5: Atomic Absorption Spectroscopy

The determination of calcium and magnesium in test samples was performed with Perkin Elmer 3110 atomic absorption (AA) spectrophotometer[15,16,17]. The flame emission method allowed magnesium to be determined with an accuracy in the order of ± 0.5 parts per million (ppm).

Samples were dissolved in dilute solutions of HCl in distilled and demineralized water. Prepared solutions were mixed and further diluted to specific dilution ratios. For magnesium, the absorption was measured at a wavelength of 285.2 nm. The Atomic Absorption machine was calibrated with several reference samples and then concentration of magnesium in test samples were analyzed.

6.5.6: Scanning Electron Microscopy (SEM)

A JEOL 840[18] scanning electron microscope was used for microstructural and microanalytical analysis of samples. This microscope operates at the range of 0.2 to 40 kV with an ultimate resolution of 4.0 nm, and a magnification range of 10x to 300,000x. It was fitted with both secondary electron and backscattered electron detectors to provide topographic and compositional images and with an energy dispersive spectrometer (EDS) for qualitative and quantitative microchemical analysis. The JEOL 840 is normally operated to magnifications of ~10,000x. Samples were coated with a layer of gold-iridium alloy in a sputtering machine and then quickly transferred inside the microscope. It was observed that in some instances morphology of samples changed due to electron beam sample interaction. As a result, magnifications less than 10,000x and low accelerating voltage, for example 10 kV, were used.

6.5.7: Laser Particle Size Analysis (LPSA)

The determination of the size distribution of particulate samples was performed with Horiba LA-920 laser particle size analyzer[19]. This system allows the measurement of a wide range of materials from 0.02 to 2,000 microns. LPSA employs the Low Angle Light Scattering (LALS), Fraunhofer diffraction, or Mie Scattering for determination of particle size. Fraunhofer diffraction is the simplest method of determining particle size from light scattering measurements. For particles larger than the wavelength of light in the beam, the light scatters from the edge of the particle at an angle, which is dependent on the size of the particle. Larger particles scatter light at relatively smaller angles than light scattered from smaller particles. From observing the intensity of light scattered at different angles, different sized particles are distinguished. Figure 29 presents a schematic principle of LPSA.

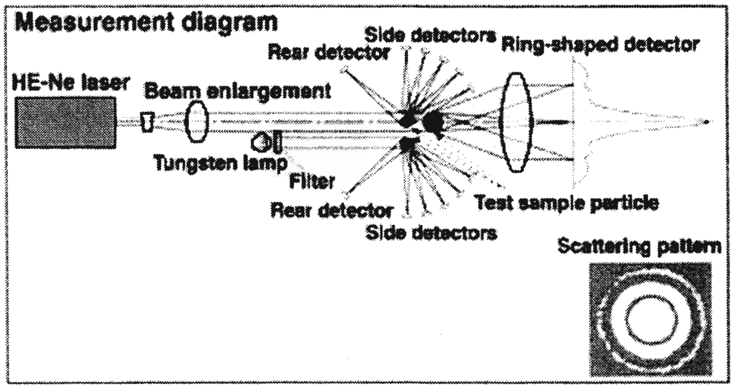

Figure 29: Principal of Laser Particle Size Analysis (LPSA).

The particle circulation system uses a high-output centrifugal pump that can circulate 2,000 μm particles smoothly and includes an ultrasonic probe to achieve optimum dispersion. Since the probe is internal, determination of size distribution can be carried out at the same time as dispersion. Samples were suspended in isopropyl alcohol and fed to the machine. Then ultrasonic disperser was used to achieve better size distribution measurements.

6.5.8: Ion Chromatography

Chlorine concentration in aqueous solutions was determined with Dionex DX-100 ion chromatograph[20]. The chlorine detection limit for Ion chromotaography was in the order of ± 0.1 parts per million (ppm). Samples were dissolved in dilute solutions of HNO_3 or H_2SO_4 in demineralized and deionized water. Samples then were diluted to specific dilution ratios. After stabilization of the equipment and calibration of the machine with several reference samples, the concentration of chlorine in each sample was measured. Each test was repeated three times to meet the desired reproducibility requirement and the average value was used.

6.6: References

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Chapter 7: Oxides in the Dehydration of Magnesium Chloride Hexahydrate

7.1: Abstract

Experiments were performed to study the composition and extent of formation and transformation of the non-equilibrium products of thermal dehydration of $MgCl_2.6H_2O$ (bischofite) upon holding at temperature under uncontrolled atmosphere. In the experiments, samples of bischofite of known mass were rapidly heated to predetermined temperatures ranging from 200 to 600 ^oC and then held at these temperatures for varying amounts of time ranging from 5 to 20 minutes before being rapidly cooled. The oxide formed was found to be poorly crystalline MgOHCl for all temperatures other than 600 ^oC where it also contained some MgO. Upon holding at temperature, it was found that the dewatering and hydrolysis occurred gradually at temperatures up to 400 ^oC and that the amount of the oxides formed from the ongoing hydrolysis increased with holding time. By contrast, the mass of oxide produced by holding at 500 and 600 ^oC peaked at around 60 seconds of holding. The peak in oxide mass at roughly one minute of holding at 500 or 600 ^oC suggested that there was an initial very rapid 'rearrangement' of the Mg, Cl, H and O atoms to produce the poorly crystalline magnesium hydroxychloride phase and it is thought that this 'primary' hydrolysis occurred to some extent at all temperatures to produce the initial poorly crystalline MgOHCl that was detected at the end of the heating time to any temperature. For convenience, the gradual dewatering and oxide formation that occurred was denoted 'conventional' hydrolysis to distinguish it from the heretofore-unreported very rapid formation of a poorly crystalline hydroxychloride upon heating to temperatures over 200 ^oC.

7.2: Introduction

The dehydration of magnesium chloride hydrates to produce anhydrous magnesium chloride containing minimal hydrolysis products is of great importance to electrolytic magnesium production processes[1] because of the highly detrimental affects of these oxygen and possible hydrogen containing compounds on the performance and productivity of the electrolysis cells. The anhydrous magnesium chloride feed used commercially is obtained by either partial or complete dehydration of aqueous magnesium chloride solutions. The control of oxide formation during the inadvertent hydrolysis that occurs during the dehydration process is a common challenge for the magnesium production industry.

The $MgCl_2$-H_2O phase diagram available in the literature[1] shows that during the dehydration of the magnesium chloride brines, bischofite (magnesium chloride hexahydrate, $MgCl_2.6H_2O$) is the first solid phase to precipitate from the aqueous solution and thus it becomes the starting material for thermal dehydration. It is well known that the dehydration of magnesium chloride hexahydrate to tetrahydrate and then to dihydrate occurs readily with the release of 2 molecules of water each time the temperature of the system is raised above the respective equilibrium temperature according to Reactions 61 and 62 shown in Table X. Table X also presents Reaction (63) showing the dehydration of magnesium chloride dihydrate to magnesium chloride monohydrate at 240 °C as well as Reaction (64)[2,3] for the decomposition of magnesium chloride dihydrate resulting in formation of MgOHCl also at 240 °C. Thus, heating magnesium chloride dihydrate to 240 °C under uncontrolled atmosphere is said to result in a process that is 'competitive' between Reactions (63) and (64)[1,4,5]. Reaction (64) has been referred to in the literature as hydrolysis[1,4,5]. It is not hydrolysis in the real sense of the word, which implies the reaction of an anhydrous salt with water, Reactions (67) and (68), but rather it is a decomposition or rearrangement of the atoms in such a way that water and HCl gas are evolved and MgOHCl is produced.

Heating above 240 °C results in behaviour which is complex to analyze because any of Reactions (63) to (69) and/or Reaction (70), which has been added for completeness, can occur depending on the local conditions of temperature, the chemical activities of the solid species and the partial pressures of the gaseous species and on the kinetics of the chemical reactions and/or local mass transfer processes. The understanding of the reactions mechanisms is further confounded by the possibility that crystalline MgOHCl may be the equilibrium form of non-equilibrium non-stoichiometric non-crystalline solid solutions of $MgCl_2$ and MgOHCl.

The present authors have taken advantage of the insolubility of magnesium oxide and magnesium hydroxychloride in methanol to isolate the oxide containing products of reaction that form upon heating bischofite over 240 °C. This way they were able to address the complexity of the present system for the purposes of developing a better understanding of the mechanisms and kinetics of the thermal removal of water from bischofite and the inadvertent hydrolysis that occurs during this thermal dehydration. Consequently, the present authors have been able to develop a description of the processes which occur when bischofite is heated in uncontrolled atmosphere without attempt to control the hydrolysis that occurs, by examining the mass loss of bischofite samples rapidly heated to different temperatures and held at these temperatures for different periods of time, as well as by examining the XRD spectra of the products of these heating and holding tests.

Table X: Dehydration Reactions and Equilibrium Temperatures in the Magnesium Chloride Water System.

	Equilibrium Temperature[‡]	Reaction
$MgCl_2.12H_2O \rightarrow MgCl_2.8H_2O + 4\,H_2O$	–16.8 °C	(59)
$MgCl_2.8H_2O \rightarrow MgCl_2.6H_2O + 2\,H_2O$	–3.4 °C	(60)
$MgCl_2.6H_2O \rightarrow MgCl_2.4H_2O + 2\,H_2O$	116.7 °C	(61)
$MgCl_2.4H_2O \rightarrow MgCl_2.2H_2O + 2\,H_2O$	182.5 °C	(62)
$MgCl_2.2H_2O \rightarrow MgCl_2.H_2O + H_2O$	240 °C	(63)
$MgCl_2.2H_2O \rightarrow MgOHCl + H_2O + HCl$	240 °C	(64)
$MgCl_2.H_2O \rightarrow MgCl_2 + H_2O$		(65)
$MgCl_2.H_2O \rightarrow MgOHCl + HCl$		(66)
$MgCl_2 + H_2O \rightarrow MgO + 2\,HCl$		(67)
$MgCl_2 + H_2O \rightarrow MgOHCl + HCl$		(68)
$MgOHCl \rightarrow MgO + HCl$	555 °C	(69)
$MgCl_2.2H_2O \rightarrow MgCl_2 + 2\,H_2O$		(70)

Previous studies on this topic were performed by Kirsh et al.[6] who studied the dehydration kinetics of bischofite ($MgCl_2.6H_2O$) and 'partially-dried bischofite' (a

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[‡] Equilibrim temperature calculated as the temperature at which partial pressure of H_2O or HCl reaches 1 atmosphere.

mixture of $MgCl_2.6H_2O$, $MgCl_2.4H_2O$ and $MgCl_2.2H_2O$) by analyzing the magnesium and chlorine contents of the solid products of the dehydration process. Kirsh et al. suggested that the processes occurring during the thermal dehydration of bischofite comprised dehydration, thermal hydrolysis, dehydrochloridization/dehydroxylation and melting. They found that heating and dehydration of the magnesium chloride dihydrate resulted in the formation of magnesium hydroxychloride according to Reaction (64) starting at 240 °C. Kirsh et al. also reported that the activation energy Reaction (64) was 205 kJ/mole and concluded that the last two molecules of water were strongly bonded to the magnesium chloride and thereby suggested that Reaction (70) was unlikely to occur.

7.3: Experimental

The present experiments aimed to determine the compounds and the assay of the products of dewatering and hydrolysis of bischofite samples heated in uncontrolled atmosphere[§] to various temperatures and held at various times at those temperatures. Other work[7] of the authors had found that due to the completion of dehydration in a very short time, it is likely that composition of resultant products not being influenced by surrounding atmosphere. As a result, it was decided to study dehydration in uncontrolled atmosphere.

It was also noticed that the rate of heating of the samples influenced the observed products of dewatering and hydrolysis, so in the present experiments, as high a heating rate as possible was used so that the effect of the transient could be reduced as much as possible.

In the present experiments, chemical grade (99.9 %) bischofite ($MgCl_2.6H_2O$) from Sigma-Aldrich was used. Approximate one gram samples of precisely known mass were placed into the hot zone of a 4 cm ID tube furnace open to the atmosphere. The samples rapidly heated to predetermined temperatures ranging from 200 to 600 °C and were then held at these temperatures for varying amounts of times ranging from 5 to 30 minutes before being removed and rapidly cooled.

[§] The humidity of air was not measured.

In practice, the samples were quickly moved into the hot zone of the furnace and the time required to heat the samples to the furnace temperature was found to be about 10 seconds from readings of a thermocouple placed in one of the sample crucibles. The resulting heating rate was in order of 1000 °C/min[**]. The time when the samples reached the desired temperature was considered to be the beginning of the decomposition process for the purposes of kinetic analysis.

The samples were removed from the furnace at regular time intervals, canned and quickly transferred to a dry glove box where the sample masses were precisely measured. A portion of each sample was then leached in ultra-pure, dry methanol to isolate and separate the insoluble magnesium oxide and magnesium hydroxychloride from the soluble magnesium chloride which resulted from dehydration and from the soluble residual magnesium chloride hydrates[8,9,10].

The oxides isolated by methanol leaching were then dried at about 100 °C, which was enough to evaporate the methanol but not sufficient to change the composition of the oxides. Thereafter, the mass of the residue was measured and examined by XRD. The retained portion of the product of the heating and holding tests was also examined by XRD to identify all species present in the products of dehydration.

7.4: Results: XRD Spectra: The Products of Dehydration

The XRD spectra for the oxides isolated from the samples heated and held at 200 °C for 10 and 30 minutes were similar. Figure 30 shows that the product of dehydration at 200 °C was a mixture of magnesium chloride monohydrate, magnesium chloride dihydrate, and magnesium chloride tetrahydrate as well as magnesium hydroxychloride, MgOHCl[7]. Since the dehydration temperature was not sufficient to remove all water in the samples, no anhydrous $MgCl_2$ was found.

[**] Heating rates were estimated based on the thermocouple readings and may be differ from actual values.

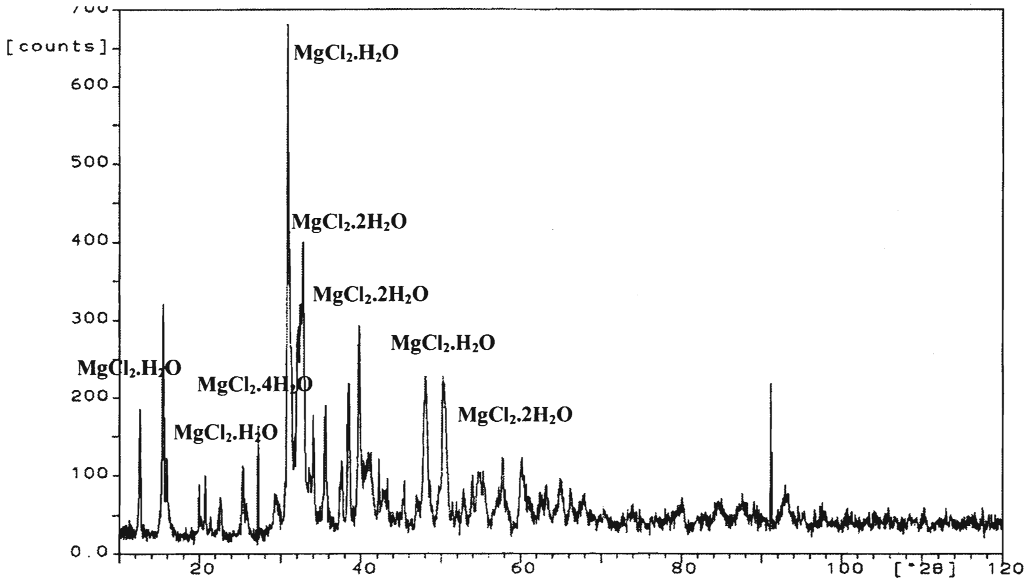

Figure 30: XRD Spectrum of the Products of Bischofite Heated and Held at 200 °C for 30 Minutes.

Figure 31 shows that when the holding temperature was increased to 300 °C, all the water in the samples was removed and resulted in the production of a mixture of anhydrous $MgCl_2$ and MgOHCl.

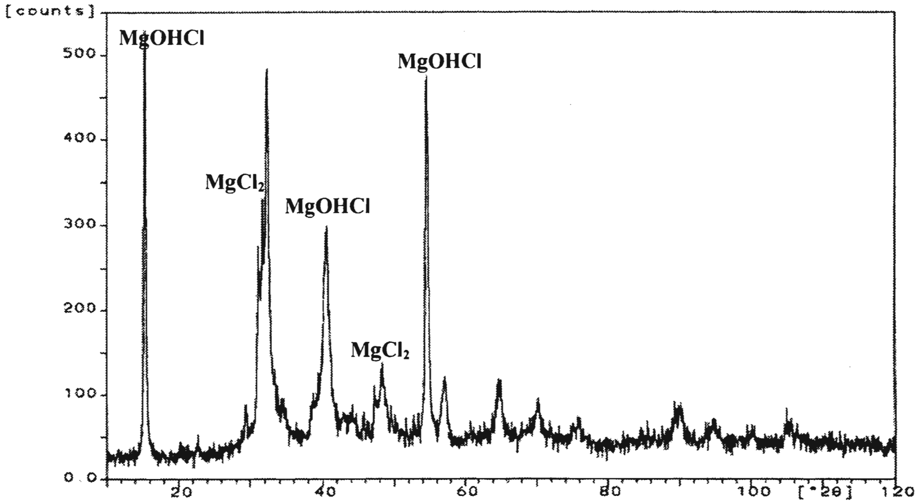

Figure 31: XRD Spectrum of the Products of Bischofite Heated and Held at 300 °C for 30 Minutes.

Figure 32 and Figure 33 show the XRD spectra of the dehydration products of bischofite from the heating and holding of the samples at 400 °C for 10 and 30 minutes. As with the samples heated at 300 °C, dehydration resulted in the production of anhydrous $MgCl_2$ and

MgOHCl. It was noted that in the sample with 30 minutes holding time, the intensity of characteristic peaks of MgOHCl was measurably increased relative to the sample with shorter holding time. This was considered as evidence for the progressive production of MgOHCl from the hydrolysis of $MgCl_2$.

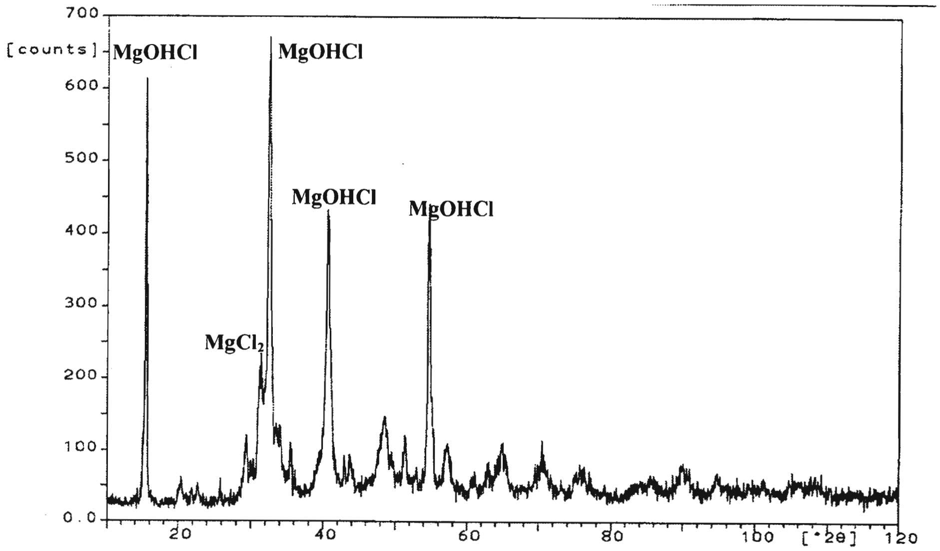

Figure 32: XRD Spectrum of the Products of Bischofite Heated and Held at 400 °C for 10 Minutes.

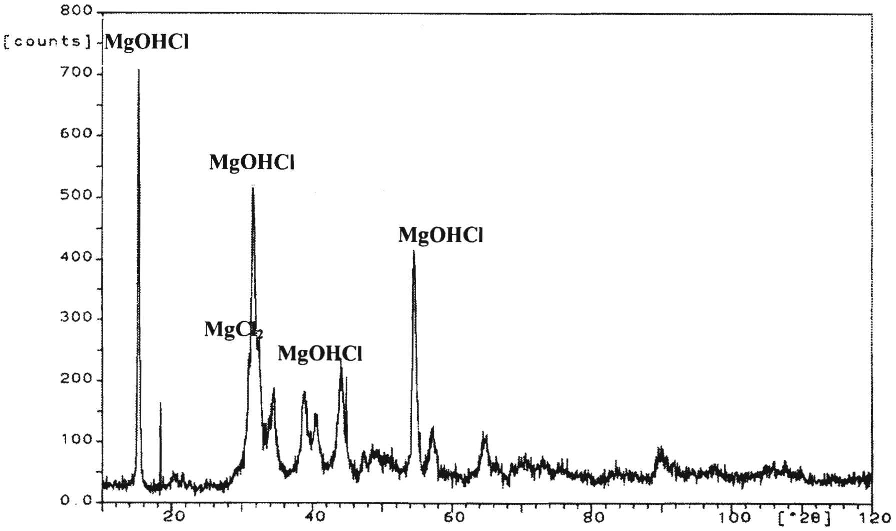

Figure 33: XRD Spectrum of the Products of Bischofite Heated and Held at 400 °C for 30 Minutes.

Figure 34 and Figure 35 show that, when the holding temperature was increased to 500 °C, a mixture of MgO, MgOHCl and $MgCl_2$ was produced. It was found noteworthy that increasing the sample holding time considerably increased the intensity of MgO characteristic peaks. This was explained by the relatively fast decomposition of MgOHCl to MgO at this temperature[11].

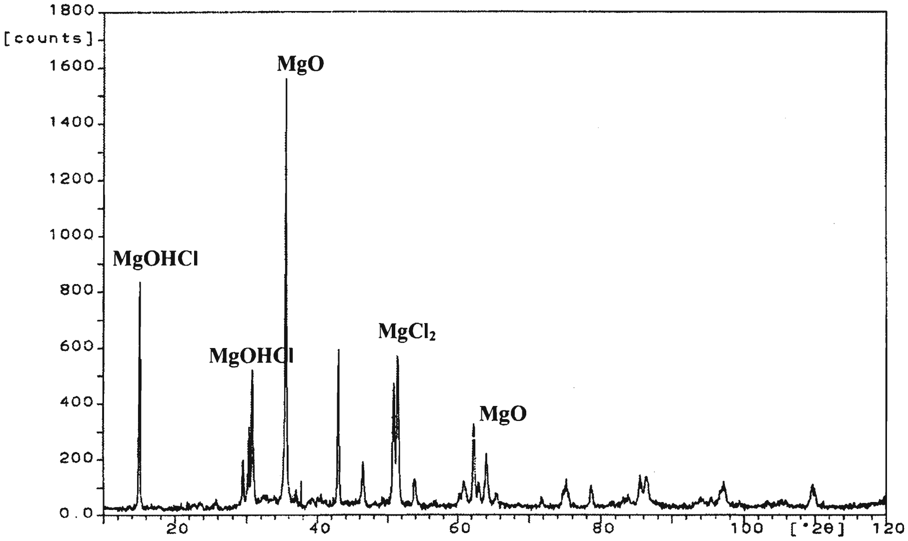

Figure 34: XRD Spectrum of the Products of Bischofite Heated and Held at 500 °C for 10 Minutes.

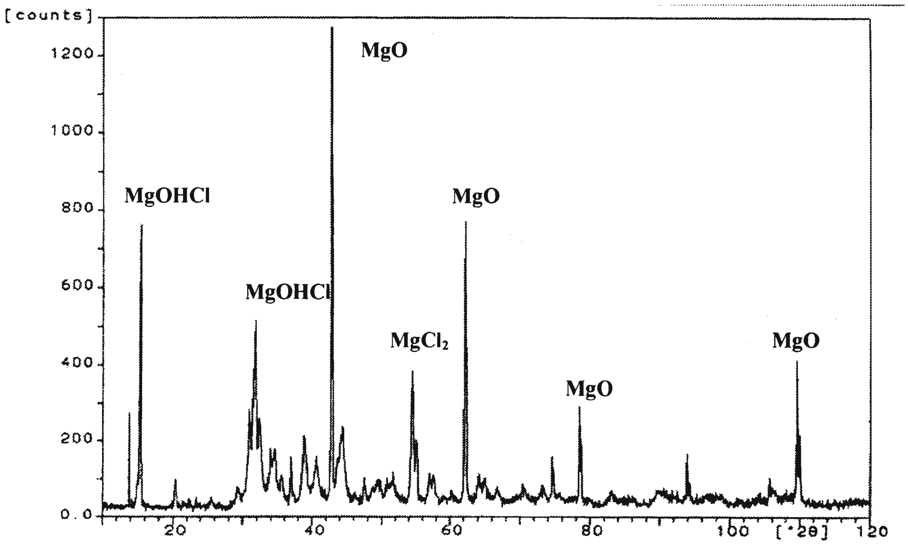

Figure 35: XRD Spectrum of the Products of Bischofite Heated and Held at 500 °C for 30 Minutes.

Figure 36 and Figure 37 show that at 600 °C, when sample was heated for 10 minutes, a mixture of $MgCl_2$ and MgO was detected but increasing in the sample holding time resulted in decreased $MgCl_2$ characteristic peaks.

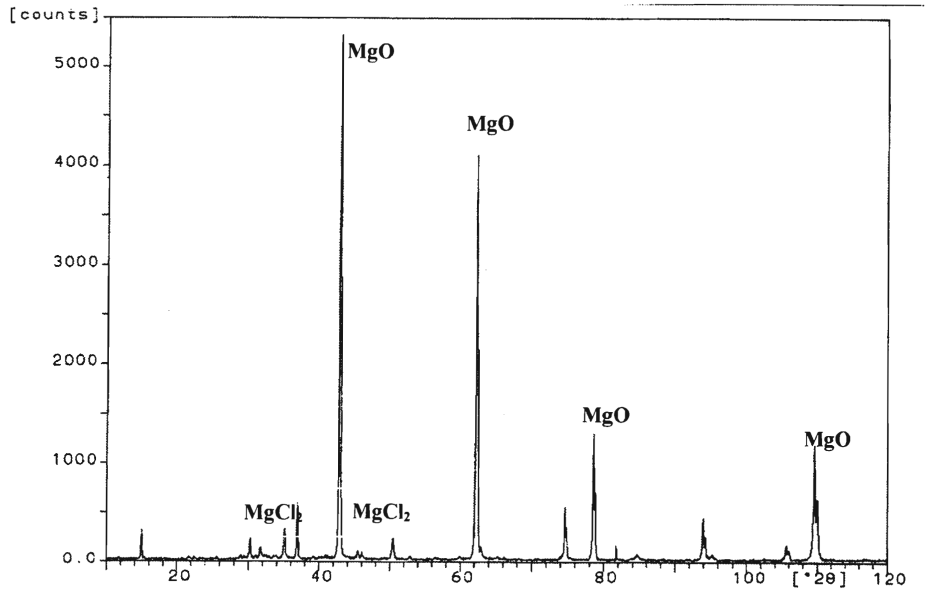

Figure 36: XRD Spectrum of the Products of Bischofite Heated and Held at 600 °C for 10 Minutes.

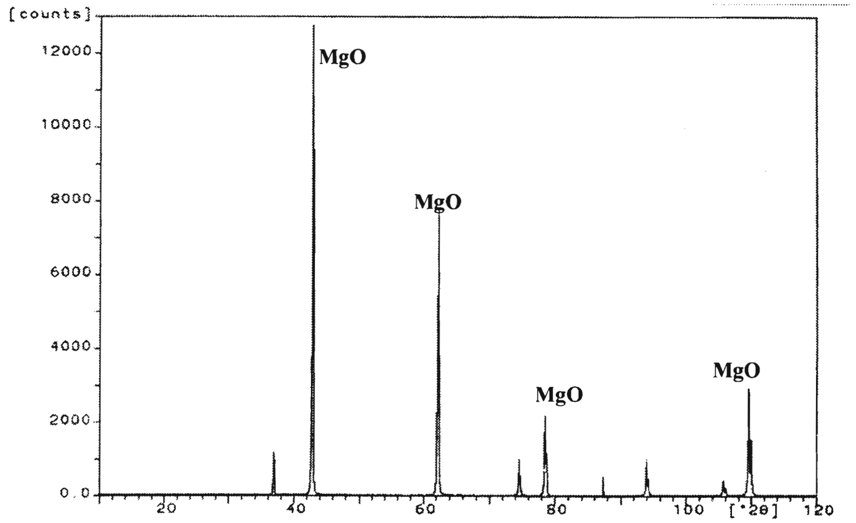

Figure 37: XRD Spectrum of the Products of Bischofite Heated and Held at 600 °C for 30 Minutes.

7.5: Results: XRD Spectra: The Oxides Isolated from the Products of Dehydration

Figure 38 presents the XRD spectra of the oxide/hydroxychloride residue resulting from the dehydration and 'hydrolysis' of bischofite with a 1000 °C/min heating rate to different temperatures. It can be seen that with this rapid heating, even to low temperatures, the residue contained only poorly crystalline hydroxychlorides, except for heating to 600 °C, when MgO was formed in less than a minute[11].

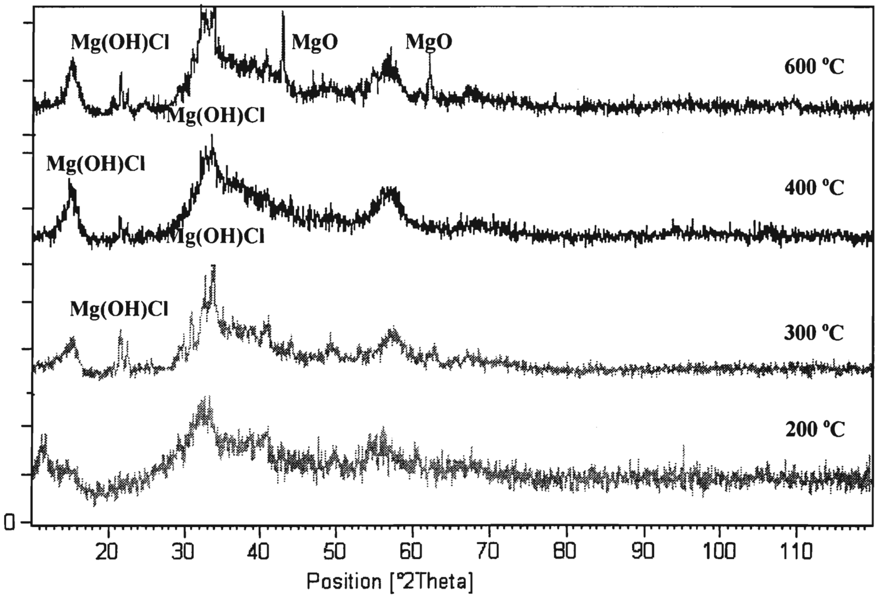

Figure 38: XRD Spectra of the Isolated Oxide Residue Resulting from the Heating of Bischofite at 1000 °C/min to Different Temperatures.

The XRD spectra for the oxides isolated from the samples heated and held at 200 and 300 °C for various holding times were essentially identical, i.e., nothing but poorly crystalline hydroxychloride was identified, Figure 39. Figure 40 presents the XRD spectra for the oxides isolated from bischofite samples heated and held at 400 °C for various lengths of time. MgOHCl was identified to be the only product of hydrolysis at this temperature.

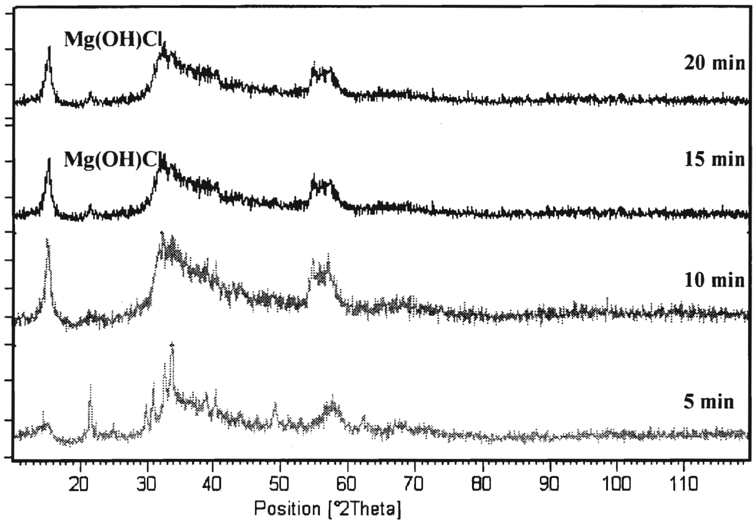

Figure 39: XRD Spectra of the Oxides Isolated by Methanol Leaching of the Products of Heating and Holding Bischofite at 300 °C for 5, 10, 15 and 20 Minutes.

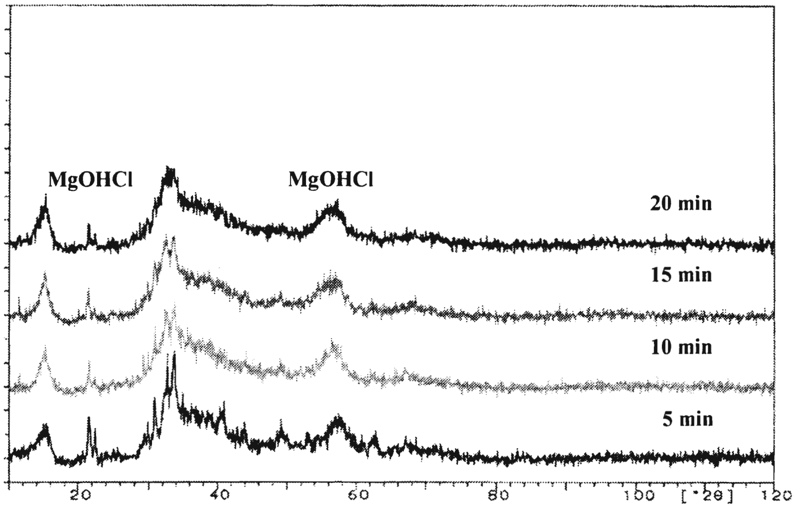

Figure 40: XRD Spectra of the Oxides Isolated by Methanol Leaching of the Products of Heating and Holding Bischofite at 400 °C for 5, 10, 15 and 20 Minutes.

Figure 41 presents the XRD spectra for the oxides isolated from bischofite samples heated and held at 500 °C for various lengths of time. It can be seen that the degree of crystallinity of the MgOHCl increased with increasing holding time and the decomposition of the MgOHCl into MgO also increased with holding time with the first MgO appearing only after 5 minutes of holding. Figure 42 presents the XRD spectra for the oxides isolated from the samples heated and held at 600 °C. It can be seen that some MgO was evident after as little as one minute of holding and the poorly crystalline

MgOHCl remaining after five minutes of holding was fully decomposed to crystalline MgO in less than 10 minutes of holding at 600 °C.

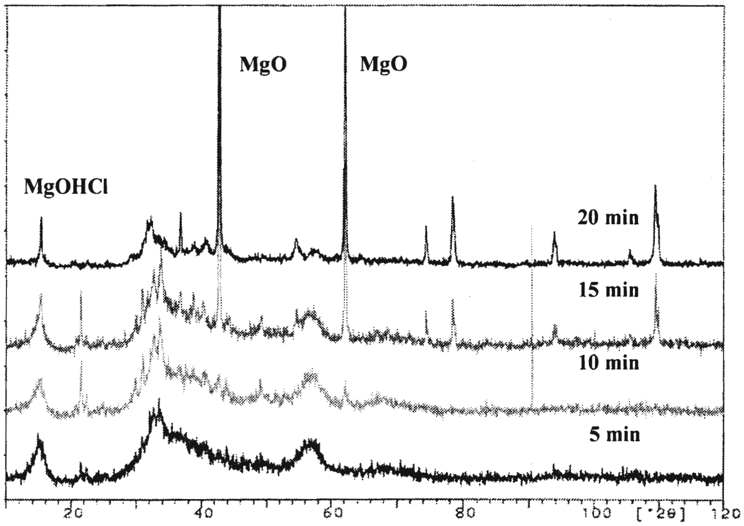

Figure 41: XRD Spectra of the Oxides Isolated by Methanol Leaching of the Products of Heating and Holding Bischofite at 500 °C for 5, 10, 15 and 20 Minutes.

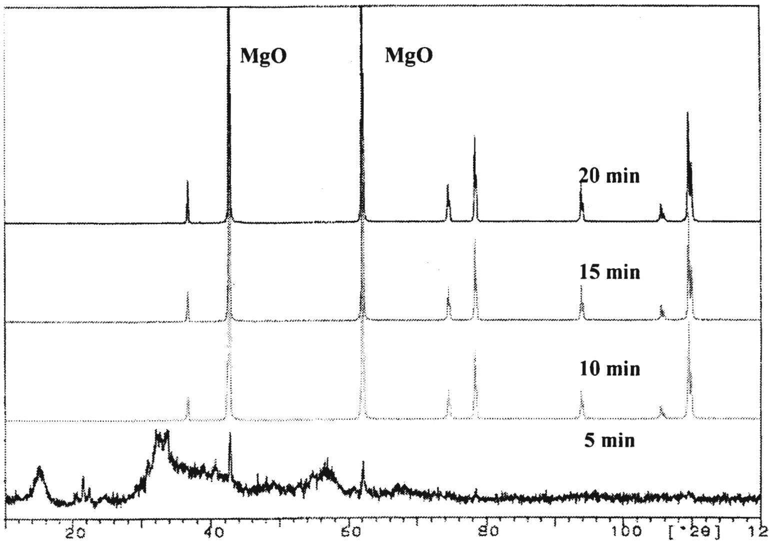

Figure 42: XRD Spectra of the Oxides Isolated by Methanol Leaching of the Products of Heating and Holding Bischofite at 600 °C for 5, 10, 15 and 20 Minutes.

7.6: Results: Masses of the Products of the Heating and Holding Tests and of the Isolated Oxides

The masses of the samples after heating and holding at temperature are presented in Figure 43. Each data point represents the average of three repeated measurements. It can be seen that the sample masses decreased as the experiments proceeded. For the samples held at 200 °C, they lost 30 % of their original mass in 30 minutes as compared to an expected 53 % lost for the complete removal of the six moles of waters.

For the samples held at 300 °C, the mass loss was 65 % at the end of the experiment and for the sample held at 400 °C, the mass loss leveled off at 65 %, the same value of the mass loss for 300 °C, but it took only 10 minutes for this loss. Because this mass loss exceeded that for complete conversion to MgOHCl (via Reactions (61) to (64) commensurate with 62 % mass loss), the mass loss result indicates that some of the MgOHCl must have formed via Reaction (65). The occurrence of Reaction (66) indicated that $MgCl_2$ was present during the test, as shown in the XRD analysis of the 30 minutes, 400 °C sample, Figure 27.

For the samples held at 500 °C and 600 °C, the final mass losses of the samples were 75 % and 79 %, respectively. Such a mass loss indicated near-complete conversion of bischofite to MgO (80 % mass loss) and was in agreement with the XRD analysis of the 600 °C sample, Figure 36 and Figure 37.

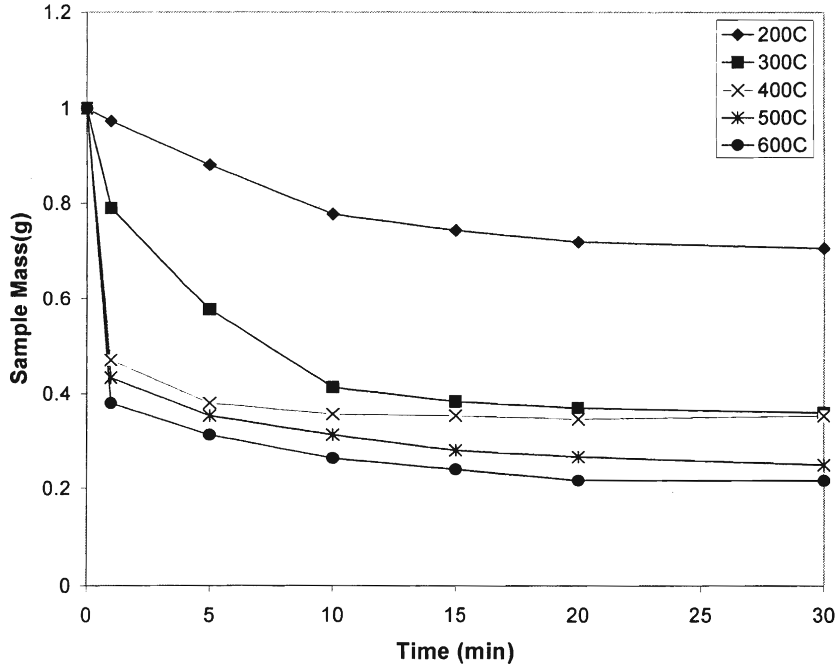

Figure 43: Masses of the Bischofite Samples after Heating and Holding for various Times at various Temperatures.

The data points are the average of three repeated tests. The estimated average uncertainty of the mass measurements was ± 0.01 g.

Figure 44 presents the mass of the residue isolated by the author's methanol leaching technique[12]. The average MgOHCl formation rates over the 30 minutes of holding at 400 °C and in the first minute of the test at 500 °C, assuming for convenience that there was no MgO formed, were 0.008 g/min and 0.22 g/min, respectively. A crude Arrhenius rate analysis indicated that the activation energy was roughly 145 kJ/mole and was roughly similar to the value found by others. The amount of oxide produced by the time the sample had reached 500 °C was 0.22 g and was a mixture of MgOHCl and MgO according to the XRD analysis, Figure 34 and Figure 35. The formation of MgO was the result of the decomposition of MgOHCl and was insufficient for the complete conversion to MgO because the decomposition of MgOHCl is not a relatively fast process[11].

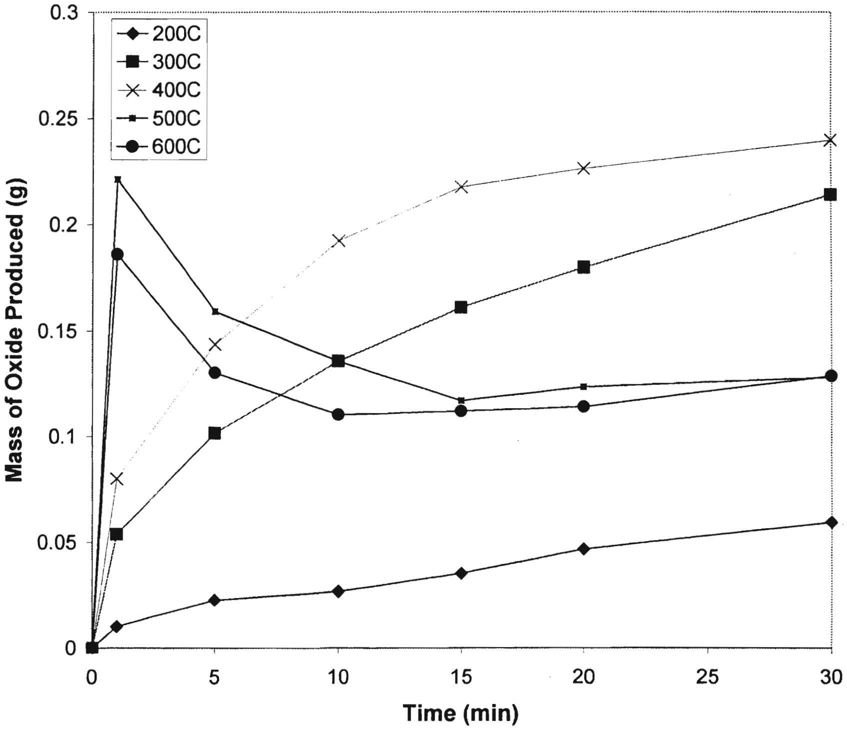

Figure 44: Mass of Oxide Residue Isolated from the Products of Heating and Holding Bischofite at various Temperatures and Times.

The estimated average uncertainty of the mass measurements was ± 0.01 g.

7.7: Discussion

7.7.1: Initial Rapid Heating

Analysis of the XRD spectra of the oxides produced in the short time it took the samples to heat, Figure 38, surprisingly discovered the presence of poorly crystalline MgOHCl as soon as the samples had reached temperatures as low as 200 °C and up to 500 °C. The presence of MgOHCl suggested that Reactions (64) and/or (66) had indeed occurred at temperatures as low as 200 °C, despite thermodynamic predictions to the contrary that these reactions, or their precursor, Reaction (63) would not have occurred until the system reached 240 °C. This very rapid production of poorly crystalline MgOHCl is herein denoted ‘primary hydrolysis’ to distinguish it from ‘conventional hydrolysis’, the reaction between an anhydrous salt and water, which is characterized by Reaction (67).

Because of the apparent high speed of this process, it is thought that this ‘primary hydrolysis’ is better conceptualized as a local ‘rearrangement’ of Mg, Cl, O, and H atoms rather than a sequence of separate steps, Reactions (61) $\Rightarrow$ (62) $\Rightarrow$ (63) $\Rightarrow$ (66) or Reactions (61) $\Rightarrow$ (62) $\Rightarrow$ (64) to produce magnesium hydroxychloride. As noted above, Kirsh et al. were the origin of the suggestion for the occurrence of Reaction (64), the decomposition/rearrangement of magnesium chloride dihydrate, but in light of the present findings, it is no longer clear how many waters of hydration are present when this ‘rearrangement’ occurs.

7.7.2: Rapid Heating and Holding: 200 °C

The mass loss measurements for the heating and holding experiments at 200 °C, Figure 43, showed that the water removal was not instantaneous. The presence of the various magnesium chloride hydrates in the products, Figure 30, indicated that Reactions (61), (62) and (63) all occurred to some extent during holding. These figures also showed that MgOHCl was present after heating and holding for 30 minutes at 200 °C and that it was more crystalline than immediately after heating, Figure 38. The explanation for this increase in crystallinity of the MgOHCl was believed to be that the product of continued ‘primary hydrolysis’ underwent some crystal structure rearrangement with holding time. An alternative explanation, the production of a more crystalline MgOHCl by Reaction

(68), was ruled out because there was no evidence of $MgCl_2$ at the end of holding. Nevertheless, Reaction (68), to produce MgOHCl from $MgCl_2$ is herein denoted 'secondary hydrolysis', to distinguish it from primary hydrolysis, characterized by Reactions (64) and (66), and 'conventional hydrolysis', characterized by Reaction (67).

7.7.3: Rapid Heating and Holding: 300 °C

The mass loss for heating and holding experiments at 300 °C, Figure 43, again showed that the water removal was not instantaneous, but unlike the tests at 200 °C, Figure 31 showed the presence of only $MgCl_2$ and MgOHCl, which was more crystalline after heating and holding at 300 °C than immediately after heating, Figure 38. The absence of any magnesium chloride hydrates indicated that Reactions (61) to (63) and (66) had progressed to completion.

Similar to the behavior at 200 °C, the increase in crystallinity of the MgOHCl is believed to be that the product of continued 'primary hydrolysis' underwent some structural refinement with the holding time. Furthermore, the presence of $MgCl_2$ and the absence of MgO in the products indicated that $MgCl_2$ and water vapor were not present at the same time, other wise Reaction (67) would have occurred. The explanation for this was believed to be that primary hydrolysis rapidly produced MgOHCl which retarded the formation of $MgCl_2$ to a time where there was insufficient water activity to produce MgO by Reaction (67) but sufficient to produce MgOHCl by Reaction (68). In other words, Reactions (64) and (66) occurred rapidly rejecting water vapor and HCl gas and at some time Reactions (63) and (65) produced anhydrous $MgCl_2$ which reacted with water vapor still being produced to form MgOHCl by secondary hydrolysis, rather than MgO by conventional hydrolysis.

Figure 39 provides additional support for such an explanation as it showed that there was only MgOHCl in the isolated residue. Figure 44 showed that the mass of MgOHCl in the isolated residue was roughly 0.2 g and accounted for approximately 50 % of the magnesium present in the original sample in agreement with Figure 31 showing only $MgCl_2$ and MgOHCl present.

7.7.4: Rapid Heating and Holding: 400 °C

The mass loss for heating and holding experiments at 400 °C, Figure 43, again showed that the water removal was not instantaneous, but faster than at 300 °C and complete well within 30 minutes of holding. Moreover, Figure 32 and Figure 33 also showed the presence of only MgOHCl and $MgCl_2$ and the explanation for this follows that of the behavior at 300 °C. Also, the mass of the isolated residues, Figure 44, roughly 0.2 g, is in line with the behavior at 300 °C and again suggests that approximately 50 % of the magnesium initially present ends up as MgOHCl after 30 minutes of holding in agreement with Figure 32 and Figure 33.

7.7.5: Rapid Heating and Holding: 500 °C and 600 °C

The mass loss for heating and holding experiments at 500 °C and 600 °C, Figure 43, showed that the initial mass loss was very rapid during the heating with only a small further mass loss during holding. The XRD spectrum, Figure 34 and Figure 35 for 500 °C, shows there is $MgCl_2$, MgO and MgOHCl present after 30 minutes and due to the different scale in the XRD spectrum for 600 °C, Figure 36 and Figure 37, it is reasonable to conclude that the same species were also present at that temperature, though likely in different proportions. Figure 44 showed that the mass of the isolated residue peaked at roughly 0.2 g by the time the samples reached their holding temperatures and then leveled out at approximately 0.1 g. The explanation for this behavior was that the rapid dewatering was almost instantaneous as was primary hydrolysis with the result that little secondary or conventional hydrolysis occurred after the initial heating. The decrease in the isolated residue mass with increasing time of holding, corresponds to the gradual conversion of MgOHCl to MgO. Figure 44 also roughly suggests that there may have been a small increase in isolated residue mass after 15 minutes of holding and if indeed this did occur, it would suggest that there was some transformed material present at the end of heating that slowly transformed and contributed to increasing the residue mass as occurred for the lower temperature tests.

7.8: Conclusions

The kinetics of water evolution and oxide formation during the thermal dehydration and hydrolysis that occurred when bischofite was rapidly heated and held at different temperatures for different times was studied by measurement of sample mass loss and measurement of the mass of the oxide isolated using a methanol-leaching technique developed by the authors. XRD analysis of the dehydration and hydrolysis products as well as the isolated oxides found that there was an initial very rapid formation of poorly crystalline MgOHCl, little or no anhydrous $MgCl_2$ produced and varying amounts of magnesium chloride tetra-, di- and mono-hydrate. The presence of MgO in the dehydrated products was the result of thermal decomposition of the MgOHCl that was produced. A significant increase in oxide formation rate was observed when the dehydration temperature was increased from 400 ^{o}C to 500 ^{o}C. Due to some uncertainty regarding the composition of oxides produced, activation energy of the reaction occurring over this temperature range roughly evaluated to be 145 kJ/mole. It was found that the dehydration of magnesium chloride hexahydrate at about 600 ^{o}C was relatively a fast process and amount and composition of oxide species formed was controlled by the kinetics of dehydration, hydrolysis and dehydroxilation. That in turn confirms that in industrial practice, kinetics, which do not appear to have been extensively studied in this system, play a major role.

7.9: Acknowledgment

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Chapter 8: Preparation of MgOHCl by Controlled Dehydration of $MgCl_2.6H_2O$

8.1: Communication

Much of the effort in research related to the electrolytic production of magnesium has been devoted to the study of magnesium hydroxychloride (MgOHCl). Moldnehauer[1] was the first to discover that MgOHCl was formed during the dehydration of magnesium chloride hydrates and via the hydrolysis of magnesium chloride. Kelley[2] and Kassner[3] studied the formation and decomposition of MgOHCl and its thermodynamic properties. Vilnyansky and Savinkova[4] found that magnesium hydroxychloride can exist in various forms with different Mg:OH:Cl ratios. This group of compounds were considered to be a solid solution of MgOHCl in $MgCl_2$ and can be represented as MgCl(OH,Cl)[5,6].

Numerous studies were conducted to examine the thermal and hydrolytic decomposition of hydroxychlorides and their impact on the magnesium production processes[7,8,9,10]. The interest in MgOHCl follows from the fact that it contributes, in a fashion similar to MgO if present in the electrolyte, to the destruction of cell components and to the interference with the electrode reactions. Thus, its presence also severely detrimental to the electrolytic production of magnesium processes.

It has been shown that MgOHCl dissolved in magnesium production electrolyte is the major constituent of the oxygen bearing compounds[12,13] in the process. In order to facilitate studies of the behavior of MgOHCl in the molten salt electrolyte and develop methods to control the MgOHCl content, it is necessary to prepare pure MgOHCl reference samples. However, due to the very strong hydroscopic nature of Mg and Cl containing compounds, little success has been achieved to date in this aspect.

Most of the methods practiced to date for the preparation of MgOHCl involved controlled dehydration of magnesium chloride hydrates under a controlled atmosphere. However, it was found that dehydration product always contained lower hydrates and anhydrous magnesium chloride in addition to MgOHCl[14]. MgO may also be formed if the dehydration temperature is not properly controlled. Moreover, the hygroscopic nature of the magnesium chloride and magnesium chloride hydrates cause moisture absorption and due to the presence of the other oxide compounds in the samples obtained, studies of the characteristics of MgOHCl are significantly compromised.

In order to perform studies on the characteristics and behavior of MgOHCl in molten salt electrolyte, it is necessary to isolate MgOHCl from the other compounds that may form during the dehydration process. Recent work by the authors has shown that this obstacle can be overcome by leaching the dehydration product with methanol[14]. Due to the fact that the solubility of MgOHCl and MgO in methanol are extremely low (12.64×10^{-4} g/100 ml and 1.46×10^{-4} g/100 ml, respectively) as compared to $MgCl_2$ (11.29 g/ 100 ml) and other $MgCl_2$ hydrates. By dissolving the dehydration products in methanol, oxides can be separated from the $MgCl_2$ and its hydrates to enable characterization of the hydroxychloride.

In order to ensure MgOHCl is the only oxide species in the product of the controlled dehydration process, the control of temperature is crucial. Thermodynamic calculations[15] and thermal gravimetric analysis (TGA) of bischofite ($MgCl_2.6H_2O$) dehydration performed in this work found that the formation of MgO occurred only when the dehydration temperature was higher than 376 °C. Therefore, the formation of MgO can be avoided by carrying out the dehydration process at around, but less than, 376 °C to assure MgOHCl is the only oxide species being produced.

However in preparing the MgOHCl sample, it was also found that as well as the dehydration temperature, the heating rate was also a factor in determining the form of magnesium hydroxychloride obtained. The XRD spectrum of the hydroxychloride sample obtained with a heating rate, 25 °C/min, is shown in Figure 45. As can be seen, this spectrum shows only a few scattered characteristic peaks of MgOHCl. However, EDX analysis of the sample revealed that this sample was composed of Mg, O and Cl. It was believed that a solid solution of MgOHCl in $MgCl_2$, as described by Vilnyansky and Savinkova[4], instead of crystalline MgOHCl, was obtained when bischofite was rapidly dehydrated.

In order to produce crystalline MgOHCl during dehydration of $MgCl_2.6H_2O$, it was found necessary to heat the bischofite slowly. In the present work, chemical grade (99.99 %) bischofite ($MgCl_2.6H_2O$) at room temperature was charged into a tube furnace. The sample's temperature was continuously increased at a rate of 5 °C per minute until 376 °C was reached. The sample was then maintained at that temperature for 30 minutes; followed rapid cooling to room temperature. The entire heating and cooling process was carried out under uncontrolled atmosphere.

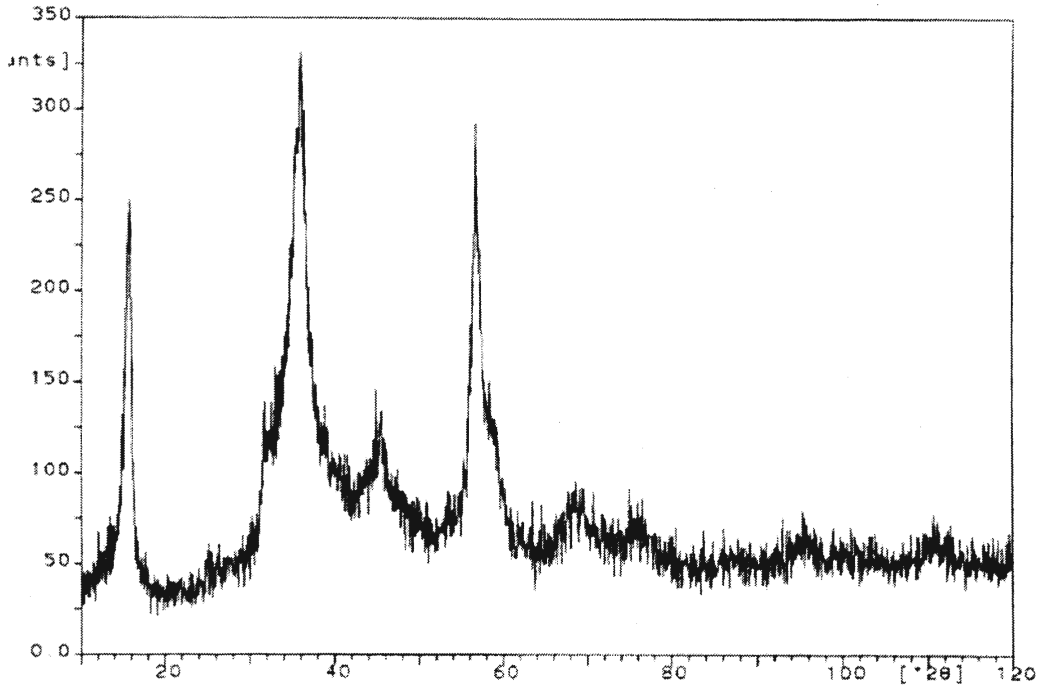

Figure 45: XRD Spectrum of Hydroxychloride Obtained with Rapid Dehydration of $MgCl_2.6H_2O$.

The sample obtained was dissolved in methanol for isolation of oxide produced. The isolated oxide was washed repeatedly with methanol to ensure all anhydrous $MgCl_2$ and $MgCl_2$ hydrates were completely removed. The fully washed sample was dried at 100 °C for evaporation of methanol and analyzed with XRD.

The XRD spectrum of the obtained sample is shown in Figure 46. It can be seen that the absorption peaks of the sample corresponded to the characteristic peaks of MgOHCl. From this result, it was concluded that crystalline MgOHCl was successfully produced by the described method.

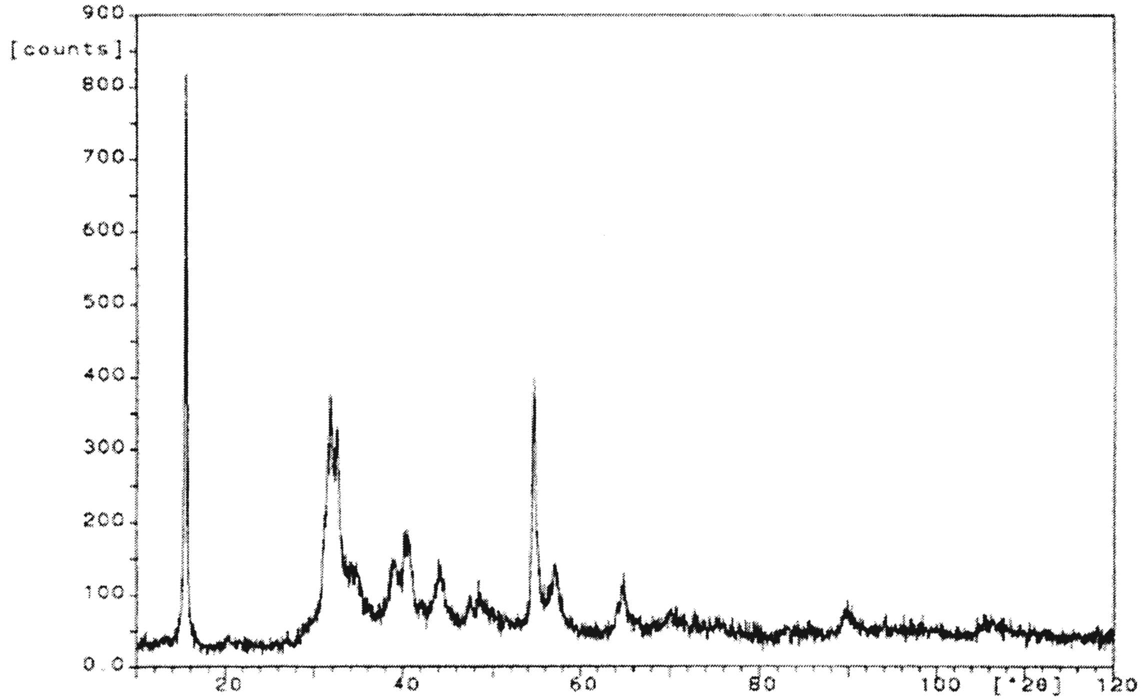

Figure 46: XRD Spectrum of MgOHCl Obtained from Controlled Dehydration of $MgCl_2.6H_2O$.

Further work was carried out to determine the purity of MgOHCl produced. The sample was dissolved in 0.1 N HCl(aq). The solution was then titrated against 0.1 N NaOH(aq) for determination of acid consumption. From the volume of acid consumed, the amount of MgOHCl in sample was determined according to the following reaction.

$$MgOHCl + HCl \rightarrow MgCl_2 + H_2O \qquad (71)$$

It was found that the mass of MgOHCl determined from the titration result represented more than 95 % of the sample mass. Based on this result, it could be seen that the purity of the MgOHCl produced in the present work was higher than 95 %.

In conclusion, high purity crystalline MgOHCl was successfully prepared by controlled dehydration of $MgCl_2.6H_2O$. The success in preparation of MgOHCl sample has considerable importance in scientific and industrial applications due to the availability of reference sample for characterization of MgOHCl physical and chemical properties.

The difficulty of isolating oxides from other dehydration products was overcome by the low solubility of MgOHCl in methanol. The formation of crystalline MgOHCl as the only oxide species during dehydration can be assured by carrying out the dehydration process at lower than 376 °C with heating rate not exceeding 5 °C per minute. The purity of the MgOHCl produced by the described procedure was found higher than 95 %.

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Chapter 9: Properties of Magnesium Hydroxychloride (MgOHCl)

9.1: Communication

The presence of oxygen bearing compounds in the fused-salt electrolyte is an important issue for electrolytic production of magnesium[1] because oxygen in the electrolyte is severely detrimental to the operation of the electrolysis cells. Thus the oxide content in the electrolyte prior to its feeding into the electrolysis cells needs to be closely monitored and controlled in order to ensure the proper operation of the electrolysis cells[2].

The current methods employed in the industry for monitoring of the oxide content in the electrolyte are based mainly on the titration of electrolyte samples with strong acid for determination of total alkalinity[3]. It has been found that oxygen in the electrolyte can be either MgO or MgOHCl[4]. Due to the lack of a reliable speciation technique for determination of MgO and MgOHCl contents of the electrolyte, the oxide content reported from total alkalinity titration can be either overestimated or underestimated depending on the assumed form of the oxygen in the electrolyte. Thus, in order to allow accurate determination of oxide content in the electrolyte, it is necessary to develop a reliable 'oxide speciation technique' that would determine the oxygen containing compounds and their amounts in a sample.

Numerous efforts have been devoted to the development of a speciation technique[5], but a common obstacle encountered by the researchers was the lack of MgOHCl reference samples for the calibration of the proposed techniques. Recent progress in controlled dehydration of $MgCl_2.6H_2O$ has enabled the preparation of MgOHCl reference samples[6]. In this article, two properties of MgOHCl are reported, namely, solubility of MgOHCl in methanol and characteristic infrared spectrum absorption peak for MgOHCl. These two pieces of information have been essential in the development of a reliable speciation technique reported elsewhere[7].

Various methods have been proposed for separation of oxides from alkali and alkaline chlorides salt such as those described by Silvilotti et al[8] and Zhang et al[9]. A common feature of these two methods is the utilization of the difference in the solubility of alkali and alkaline chlorides and their oxides in methanol. $MgCl_2$ and $CaCl_2$ have relatively high solubility in methanol, 11.29 g/100 cm^3 and 19.90 g/100 cm^3, respectively, while NaCl and KCl solubilities are limited, 1.098 g/100 cm^3 and 0.395 g/100 cm^3, respectively. In contrast, the solubility of MgO in methanol is extremely low, 1.46×10^{-4} g/100 cm^3. Upon dissolution in methanol, the chlorides and oxides in the sample can be separated by standard solid-liquid separation methods. Accurate knowledge of the solubility of MgOHCl in methanol is needed when applying in the methanol leaching technique to the separation of oxide species from a molten salt electrolyte sample.

It has been shown that MgOHCl is the major constituent of the oxygen bearing compounds in magnesium production electrolyte[10,11] and if the above-mentioned methanol leaching technique is employed for isolation of oxide species, one has to assume that the solubility of MgOHCl in methanol is low as compared to chlorides. However, the solubility of MgOHCl has never been measured and the underlying assumption of the low solubility of MgOHCl in methanol[8,9] has never been validated.

The lack of information on solubility of MgOHCl in the methanol arose from the difficulty in preparation of pure MgOHCl due to the hygroscopic nature of MgCl (OH, Cl) compounds. Recent progress in the study of $MgCl_2$ hydrates dehydration kinetics, has enabled successful preparation of pure MgOHCl samples[6,12]. It was found that MgOHCl sample could be obtained from controlled dehydration of chemical grade (99.99 %) bischofite ($MgCl_2.6H_2O$) at around 400 °C. XRD spectrum of the prepared MgOHCl sample is shown in Figure 47.

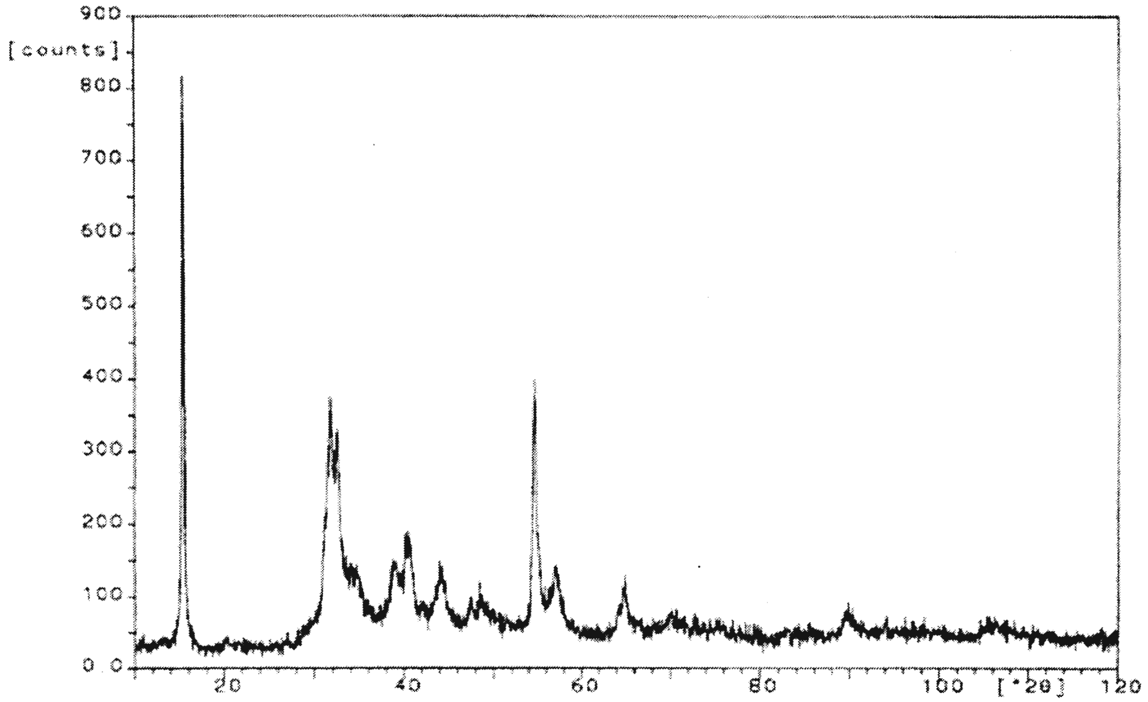

Figure 47: XRD Spectrum of MgOHCl Sample Produced by Controlled Dehydration of Bischofite.

In the solubility tests, the pure MgOHCl sample was washed with methanol repeatedly to ensure any residue $MgCl_2$ in the sample was removed. Then standard solubility tests were performed and Mg^{2+} concentrations in the methanol were measured with the Atomic Absorption (AA) technique. The results of these tests indicate that solubility of MgOHCl in the methanol is 1.26×10^{-3} g/100 ml. As can be seen, the solubility of MgOHCl is roughly 10 times higher than MgO but it is low compared to the solubility of $MgCl_2$.

It is known that the characteristic IR absorption peak of a hydroxyl group beaing compound occurs at around 3600 cm^{-1}[13,14]. Depending on the atoms bonded to the hydroxyl group, the wave number of the hydroxyl ion characteristic absorption peak may sightly vary. Due to the fact that MgOHCl is an hydroxyl group bearing compund, the existance of MgOHCl in the electrolyte sample should provide the possibility of MgOHCl characterization with IR spectrometery. Lamy[10] applied this technique in the characterization of fused salt electrolyte samples, but due to the interference of abosrbed water, he could not distinguish the charcteristic absorption of hydorxychlorides. The available of MgOHCl reference sample has allowed continuation of Lamy's work.

Here, the mulling technique was employed due its simplicity[15]. Flourolube was used as the mulling agent since its absorption peaks are located in the small wave length number region of the IR spectrum far from that of the hydroxyl group of interest here.

IR spectra acquisition was performed using a Bruker IFS66 spectrometer[16]. The system comprised a DTGS detector[16] equipped with a KBr window. This type of window covers mid-range infrared from 4000 to 400 cm^{-1}. Data treatment was performed using OPUS V 2.2 software[16]. Several replicates of the pure synthetic MgOHCl samples were tested and it was found that all obtained spectrums showing a major absorption peak at 3550 cm^{-1}. A typical spectrum is shown in Figure 48, which can now be used for qualitative analysis for samples for MgOHCl content.

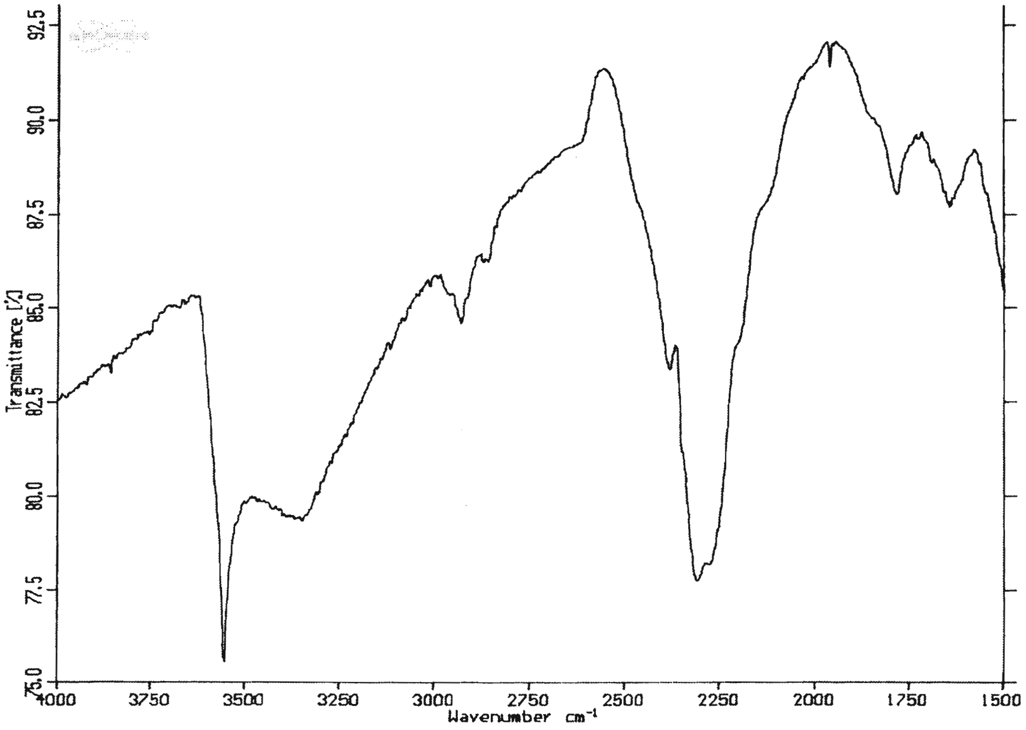

Figure 48: IR Spectrum of the Synthetic MgOHCl.

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Chapter 10: MgOHCl Thermal Decomposition Kinetics

10.1: Abstract

It was reported that MgOHCl is the major oxide species produced during the dehydration and dissolution of magnesium chloride hydrates when contacting with the spent electrolyte in the electrolytic magnesium production process. However, thermodynamic data suggested that MgOHCl should be decomposed into MgO and HCl at the operating temperature of the electrolyte. In this work, the kinetics of thermal decomposition of MgOHCl was studied. Thermal gravimetric analysis revealed that the decomposition of MgOHCl commenced at 376 °C in one step and directly converted into MgO and HCl without undergo any intermediate stage. Kinetic data shown that the thermal decomposition of MgOHCl is a first order kinetic process and the removal of the produced HCl gas was an important factor governing the rate of the decomposition. It was also found that the time required to completely decompose MgOHCl into MgO at the operating temperature of the electrolytic magnesium production process is significantly longer than the observed dissolution time of the feed materials. In results, MgOHCl produced during dehydration of the $MgCl_2$ feed is very likely not being decomposed by the heat of the surrounding electrolyte and enter the electrolyte as a dissolve species.

10.2: Introduction

Magnesium chloride hydrates are feed for many electrolytic magnesium production processes[1,2,3,4]. They are added to the fused salt electrolyte for increasing the magnesium chloride content in the spent electrolyte returning from the electrolysis cells. Final dehydration of these hydrates occurs during the contact of the feed with the fused salt at about 600-650 °C. It is found that a considerable amount of MgOHCl is produced in this process and reported to the electrolyte[5,6]. It is also known that magnesium hydroxychloride dissolved in the fused salt electrolyte are the major oxygen bearing compounds in this system. Alike MgO, magnesium hydroxychloride also contribute to the destruction of cell components and interfere with the electrode reactions[7,8,9,10,11,12] when presence in the electrolyte.

Moldnehauer[13] was the first one that discovered MgOHCl is formed through the dehydration of magnesium chloride hydrates and the hydrolysis of magnesium chloride. Kelley[14] and Kassner[15] studied the formation and decomposition of MgOHCl and its thermodynamic properties. Thermal and hydrolytic decomposition of hydroxychlorides were also studied by many other researchers[16,17,18,19,20,21].

Thermodynamically, MgOHCl decomposes to HCl and MgO when at a temperature above 555 °C[14,22].

$$MgOHCl_{(s)} = MgO_{(s)} + HCl_{(g)} \qquad (72)$$

Thus, MgOHCl should not exist at the operating temperature of the electrolytic magnesium production processes (600-650 °C). Nevertheless, it has been found that considerable amount MgOHCl being produced in final dehydration of the feed can survive into the electrolyte[5]. In order to provide insight on the survival of MgOHCl in the hot electrolyte, it is necessary to examine the kinetic of MgOHCl thermal decomposition.

10.3: Preparation of MgOHCl Reference Sample

Due to the difficulties in the preparation of reference MgOHCl samples arising from the hygroscopic nature of Mg and Cl bearing compounds, reliable kinetic data for the decomposition of MgOHCl is not available. Recent progress in the study of $MgCl_2.6H_2O$ dehydration kinetic has enabled preparation of MgOHCl reference sample. Reference samples of MgOHCl were prepared by the controlled dehydration of chemical grade (99.99 %) bischofite ($MgCl_2.6H_2O$) at about 400 °C. The chosen temperature assured the only oxide species produced during the dehydration process was MgOHCl. The dehydration product was then leached with methanol to separate $MgCl_2$ from the MgOHCl that was formed. The MgOHCl that was produced was analyzed with XRD and McGill speciation technique[23] to assure the quality of produced material. XRD spectrum and SEM image of produced MgOHCl are presented in Figure 49 and Figure 50 respectively.

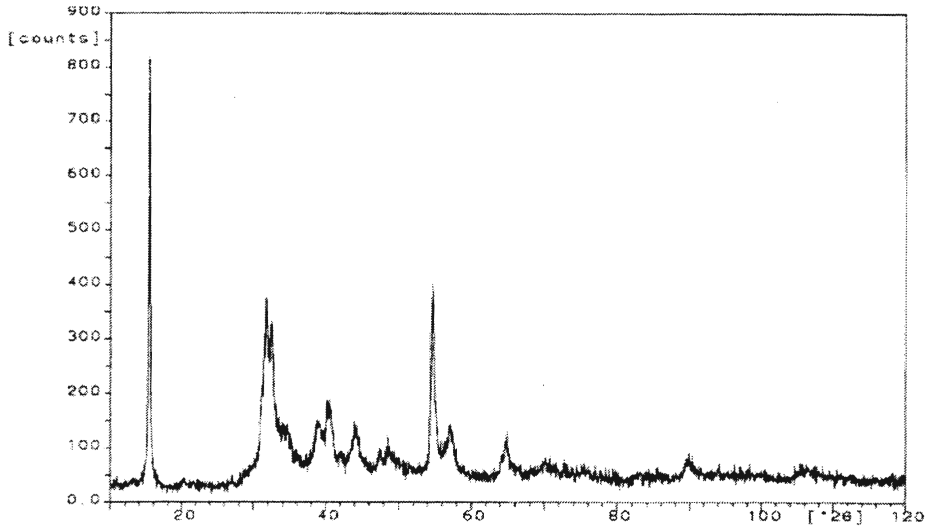

Figure 49: XRD Spectrum of MgOHCl Produced by Controlled Dehydration of Bischofite.

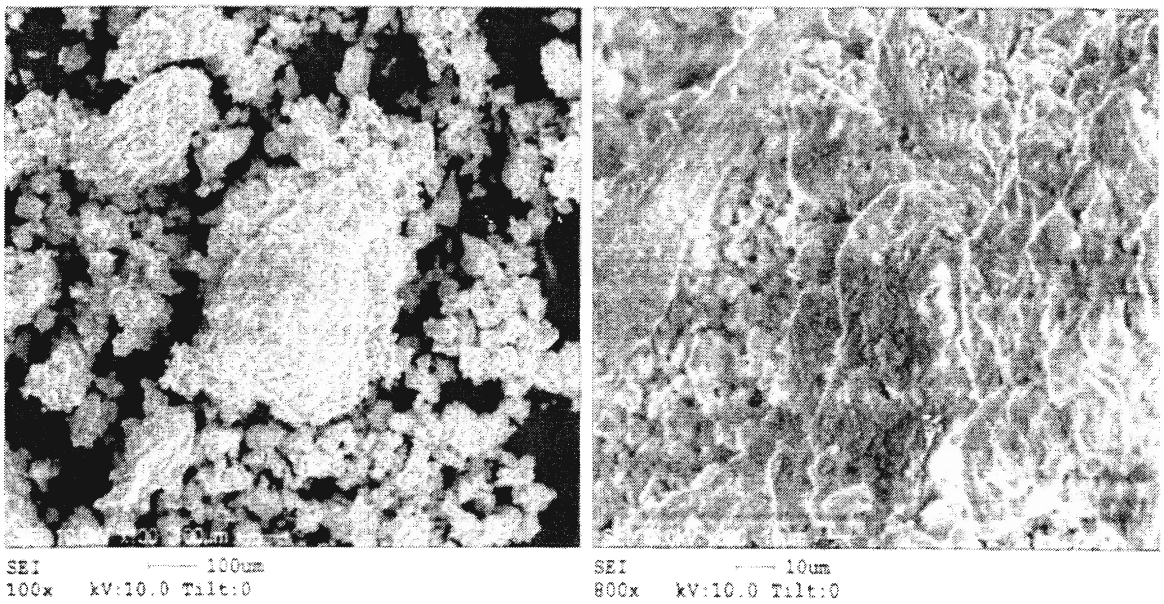

Figure 50: SEM Image of MgOHCl Produced by Controlled Dehydration of Bischofite.

10.4: Thermal Gravimetric Analysis

With the produced MgOHCl reference samples, thermal gravimetric analysis of MgOHCl was performed with a 'Cahn thermo 700 TGA' machine 0.114 g of MgOHCl sample at room temperature was charged to a high alumina crucible and then the furnace was purged with ultra pure dry helium. The sample was heated up to 600 °C with the heating rate of 10 °C/min, kept at 600 °C for 30 min and followed by natural cooling. The mass change of the sample is presented in Figure 51. It was observed that the thermal decomposition of MgOHCl occurred at 376 °C. XRD analysis of the final decomposition product revealed that MgOHCl directly decomposed into MgO without undergoing any intermediate stage.

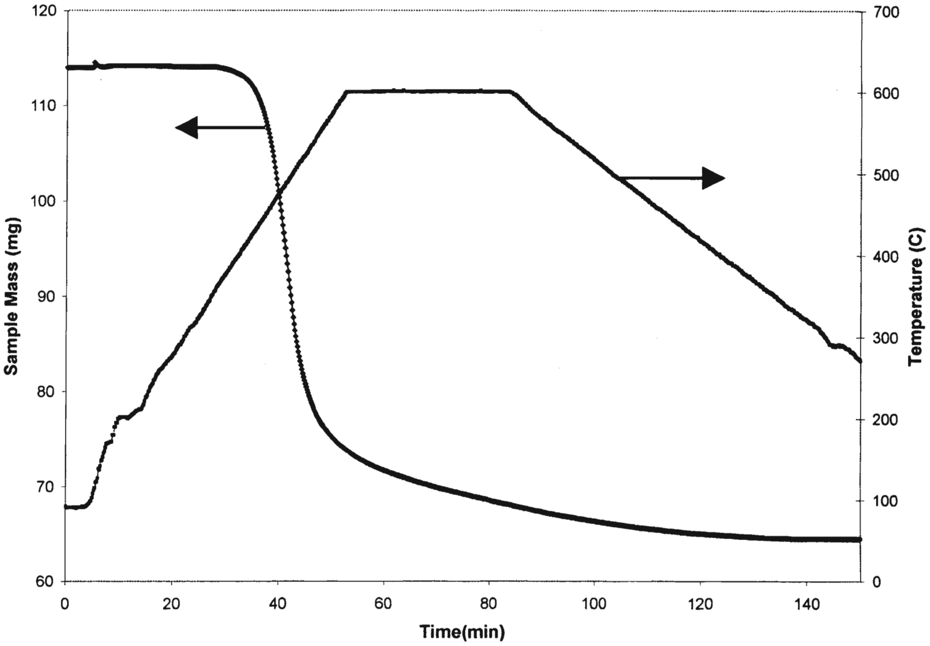

Figure 51: TGA Graph of MgOHCl Decomposition.

10.5: Isothermal Decomposition of MgOHCl

Isothermal decomposition of MgOHCl was carried out at 500, 550 and 600 °C. The temperatures chosen were sufficiently higher than the minimum decomposition temperature determined in the TGA experiments for assuring the samples could be mostly decomposed into MgO and HCl within 30 minutes. In each experiment, 6 samples of MgOHCl (1 g each) held in high alumina crucibles were placed into a furnace kept at the desired temperature. The time required to heat up the sample was found about 10 seconds. The instant when the samples reached the desired temperature was considered as the beginning of the decomposition process. Then, samples were removed from the furnace at regular time interval. The removed samples were canned and quickly transferred to a dry glove box and the sample masses were then precisely measured and analyzed by XRD.

XRD analysis of the samples revealed that the MgOHCl gradually decomposed into MgO. The XRD spectrum of samples processed at 500 °C for different time is shown in Figure 52 for illustration of the conversion of MgOHCl into MgO. As can be seen, the characteristic peak of MgOHCl gradually diminished as processing time increased and eventually completely converted into MgO.

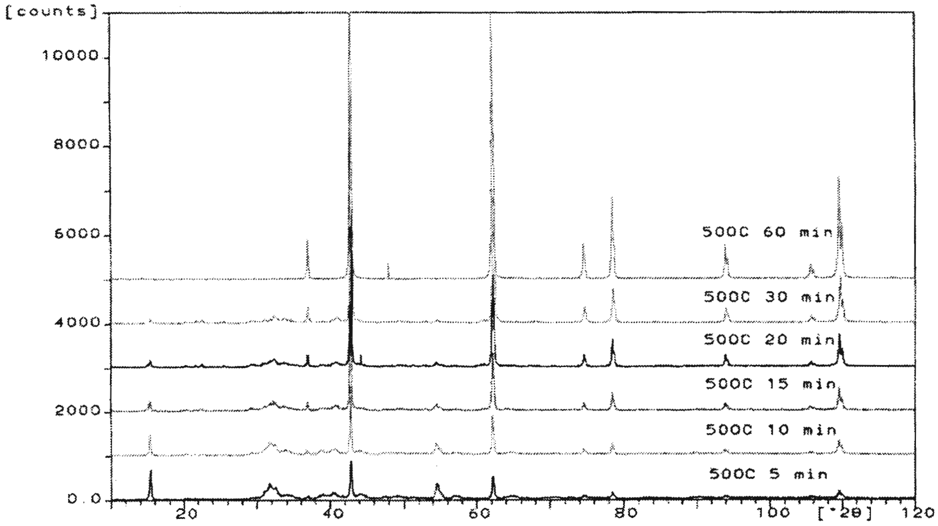

Figure 52: XRD Spectrum of MgOHCl Decomposition Product at 500 °C.

The mass lost of the sample observed during the decomposition process was due to the release of HCl gas. Therefore, the percentage of MgOHCl remaining in the sample could be determined from the mass lost data. It is worth to mention that the wt% MgOHCl reported is with respect to the original mass of MgOHCl in the sample rather than with respect to the remaining sample mass. In Figure 53, a first order kinetic plot of the experimental results is shown. Each data point represents the average of three repeated measurements. As can be seen, a linear relationship was obtained and confirmed that the kinetics of decomposition of MgOHCl is first order. Reaction rate constants were extracted from the best-fit line in Figure 46 and an Arrhenius plot was drawn as shown in Figure 54.

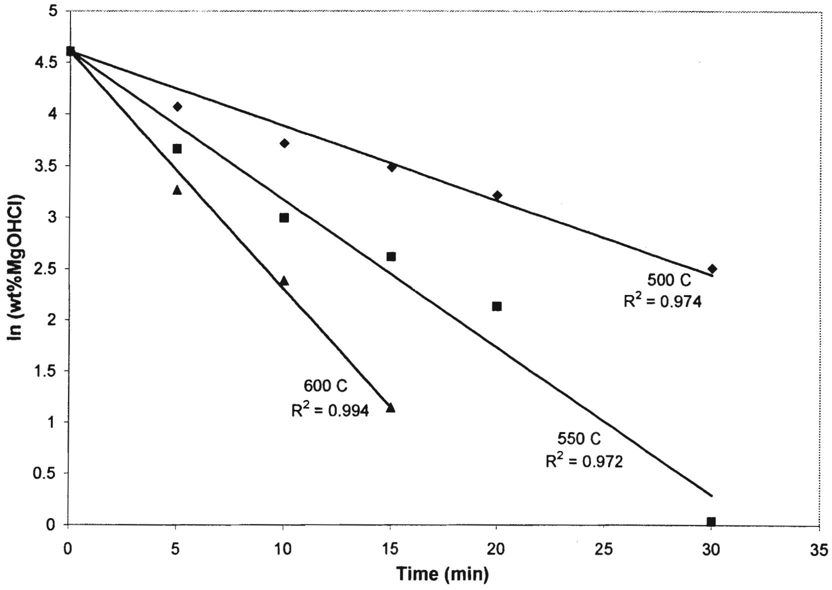

Figure 53: Kinetic of MgOHCl Thermal Decomposition.

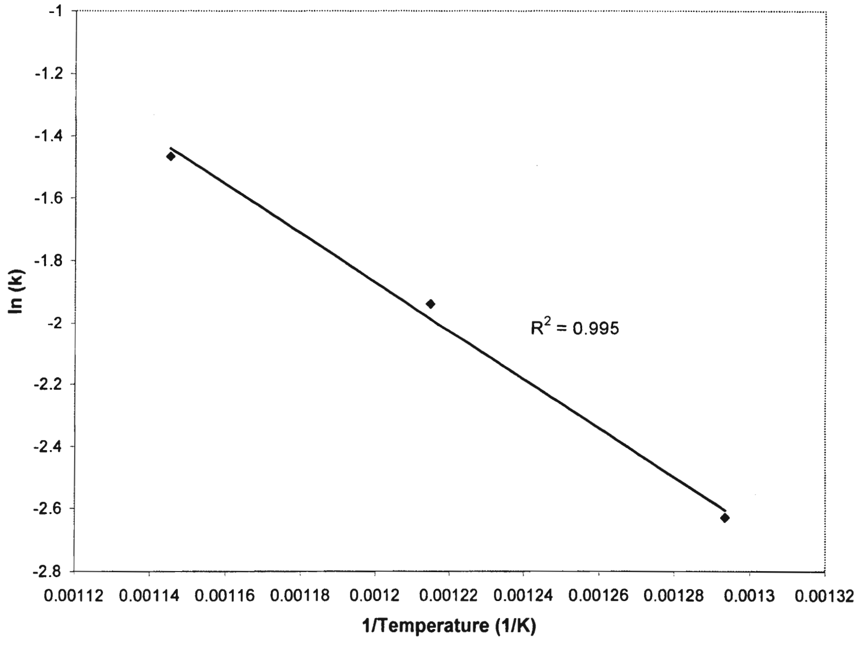

Figure 54: Arrhenius Plot of Thermal Decomposition of MgOHCl.

From the best-fit line in Figure 54, the decomposition rate constant is found related to temperature by the follow relationship.

$$\ln k = -7868\frac{1}{T} + 7.6 \qquad (73)$$

Using the information obtained, the decomposition kinetics of MgOHCl at various temperatures was computed and shown in Figure 55. As can be seen in Figure 48, it required about 10 minutes to fully decompose the MgOHCl produced during the dehydration of the hydrated $MgCl_2$ feed even at 700 °C. The time required for complete decomposition is significantly longer than the time required for dissolution of the feed in the electrolyte observed[5]. It is likely that the MgOHCl produced dissolve into the electrolyte instead of decompose into MgO and resulted in the survival of MgOHCl in the electrolyte[††].

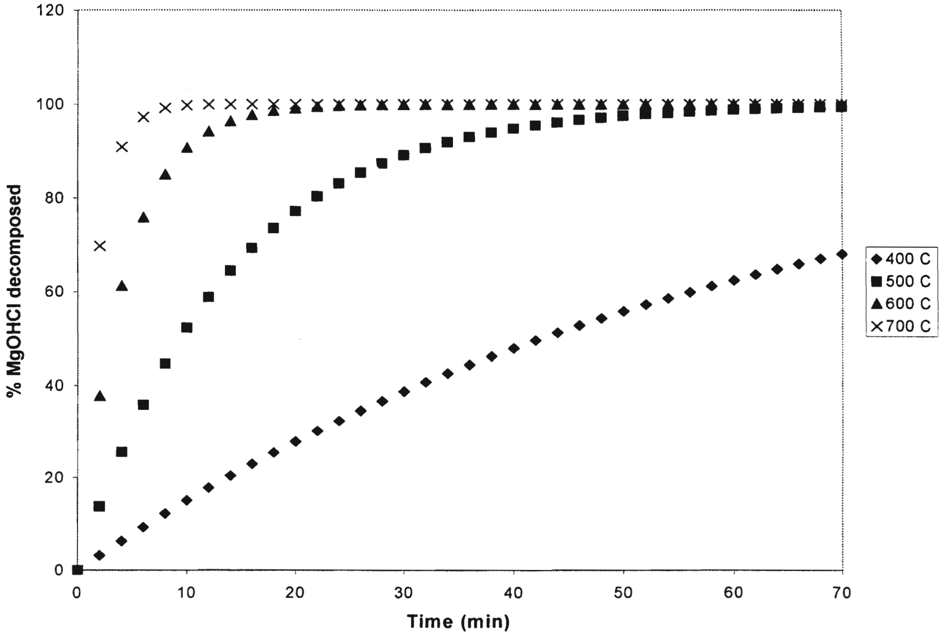

Figure 55: Decomposition Kinetics of MgOHCl at various Temperatures.

[††] The solubility of MgOHCl is function of temperature and $MgCl_2$ activity in molten salts, See Section 4.6:.

One of the products of the thermal decomposition of MgOHCl is HCl gas. It was suspected that the kinetics of the thermal decomposition of MgOHCl was controlled by the removal rate of the HCl from the sample surface. In order to validate this hypothesis, isothermal decomposition experiments at 500 °C were repeated. In these experiments, the furnace chamber was continuously purged with inert gas (Ar) at different flowrates to enhance the mass transfer of HCl gas from the sample surface. The decomposition rate constants were compared with the one under static gas atmosphere as shown in Table XI.

Table XI: Enhancement of Decomposition Kinetics by Inert Gas Purging.

Inert Gas Flowrate (m^3/s)	Decomposition Rate Constant
0	0.072
33×10^{-7}	0.111
67×10^{-7}	0.148

As can be seen, the decomposition rate constant increased by more than 50 % when the furnace chamber was purged with Ar at 33×10^{-7} m^3/s and the rate constant increased by more than 100 % as the gas flowrate increased to 67×10^{-7} m^3/s. From these results, it was concluded that the removal of HCl gas from the MgOHCl sample surface was an important factor governing the rate of decomposition.

10.6: Conclusion

Kinetic of thermal decomposition of MgOHCl was studied. It was found that the decomposition of MgOHCl commenced at 376 °C in one step and directly converted into MgO and HCl without undergo any intermediate stage. Kinetic data revealed that the thermal decomposition of MgOHCl is a first order kinetic process. Moreover, the removal of the produced HCl gas was found an important factor governing the rate of the decomposition. With the obtained information on MgOHCl decomposition kinetics, it was found that more than 10 minutes was needed to fully decompose MgOHCl into MgO at the operating temperature of the electrolytic magnesium production process, i.e. 600-650 °C. In results, MgOHCl produced during dehydration of the $MgCl_2$ feed is very likely not being decomposed by the heat of the surrounding electrolyte and enter the electrolyte as a dissolve species.

10.7: Acknowledgement

The authors wish to acknowledge the financial support of the National Science and Engineering Council of Canada and Noranda Inc. Through CRD Projects CRDPJ 2452600-00 and Noranda Technology Center Magnesium Group for their enthusiasm and support of student learning. Assistance of Mr. Patrick Blonde in the lab works is also gratefully acknowledged.

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Chapter 11: $Mg_2(OH)_3Cl.2H_2O$ Thermal Decomposition Kinetics

11.1: Abstract

The kinetics of the thermal decomposition of samples of $Mg_2(OH)_3Cl.2H_2O$ that were obtained by a novel leaching technique applied to a commercial magnesium electrolysis feed were investigated under uncontrolled atmosphere. Thermogravimetric (TG) Analysis showed that decomposition of $Mg_2(OH)_3Cl.2H_2O$ exhibited a single intermediate stage wherein crystalline water was lost at roughly 108 °C. Conversion of the resulting $Mg_2(OH)_3Cl$ to MgO, HCl and H_2O occurred at temperatures above 398 °C. Thermal decomposition of anhydrous $Mg_2(OH)_3Cl$ was seen to be consist of two stages. Both stages exhibit first order kinetics with respect to the weight percent of $Mg_2(OH)_3Cl$ remaining in the sample. However, the rates of decomposition in the two stages were significantly different. Detailed analysis of the kinetic data suggested that the rate of decomposition of $Mg_2(OH)_3Cl$ was controlled by the rate of removal of the gases released. The change in decomposition rate during the course of the experiments was explained by HCl being released in stage 1 and followed by release of H_2O in stage 2.

11.2: Introduction

The feed for commercial electrolytic magnesium production processes is either nominally anhydrous magnesium chloride or partially dehydrated magnesium chloride[1,2,3,4]. The feed is added to a fused salt electrolyte to increase the magnesium chloride content of the spent electrolyte returning from the electrolysis cells in the process. Dissolution and dehydration of the feed, the latter if partially dehydrated $MgCl_2$ is used, occurs during the contact of the feed with the fused salt at about 600 to 650 °C. The feed materials are usually prepared from dehydration of saturated magnesium chloride brines in fluid-bed dryers in which the aqueous solvent is removed, first to precipitate magnesium chloride hexahydrate, and then to remove waters of crystallization until a particular level of moisture, which depends on the process considered, is reached. The oxide produced in the dehydration process is a poorly crystalline substance that is variably described as mixtures of $Mg(OH)_2$ and $MgCl_2$ or MgO, $MgCl_2$ and H_2O as well as the tetrahydrate variant. Kirsh et al.[5] studied the kinetics of thermal decomposition of non-dried and partly dried $MgCl_2.6H_2O$ in uncontrolled atmosphere using thermal gravimetric methods (DTA, TG, DTG) and characterized the dehydration products using IR, XRD and chemical analysis of Mg and Cl. They reported that the infrared spectra of samples heated to 270 or 400 ^oC exhibited very intense OH bands. They concluded that several varieties of $Mg_2(OH)_3Cl.nH_2O$ (without a specific amount of hydration) were formed during the thermal decomposition and that these compounds exhibited a very low degree of crystallinity. Kirsh et al. also found that these amorphous phases were surface active. Chaudhuri et al.[6] characterized five hydroxychlorides in the system: $MgO\text{-}MgCl_2\text{-}H_2O$, namely: $Mg_{10}(OH)_{18}Cl_2.5H_2O$ (9-Phase), $Mg_3(OH)_5Cl.4H_2O$ (5-Phase), $Mg_2(OH)_3Cl.4H_2O$ (3-Phase), $Mg_3(OH)_4Cl_2.4H_2O$ (2-Phase) and MgOHCl(1-Phase). Chaudhuri et al. also studied the decomposition characteristics of these magnesium hydroxychloride phases using thermogarvimetry and found decomposition of these species followed first order kinetics. Kassner[7] reported formation of $Mg_2(OH)_3Cl.4H_2O$ during dehydration of magnesium chloride hexahydrate in a $HCl\text{-}H_2O$ atmosphere. Herbstein et al.[8] used high temperature in-situ, X-Ray diffractometery to characterize the thermal dehydration products of magnesium chloride hexahydrate in different atmospheres and identified $Mg_2(OH)_3Cl.4H_2O$ as one of hydrolysis products formed during the thermal dehydration of bischofite. Chahan[9] also reported formation of 'Phase-3' during thermal dehydration of magnesium chloride hydrates in the range of 250 - 400 ^oC.

In most of the previous work, the focus has been on the role of these compounds on the adhesiveness of castable refractory materials. Thus there is no thermodynamic information on these magnesium hydroxychloride phases. The present authors ongoing work of isolating the various compounds likely to form during fluid-bed drying of feeds for commercial magnesium electrolysis has demonstrated that $Mg_2(OH)_3Cl.2H_2O$ with a very low degree of crystallinity is found in the industrial feed materials that were studied[10]. The thermal stability of this oxide species is important to the industry since its decomposition and dissolution products, which form when contacted with the hot electrolyte, report directly to the electrolyte and may contribute to the destruction of cell components and interfere with the electrode reactions[11].

In the present work, $Mg_2(OH)_3Cl.2H_2O$ was isolated from the feed material of a commercial electrolytic magnesium production process as described below and the kinetics of its thermal decomposition were examined. The novel isolation process exploits the difference in solubility of magnesium chloride hydrates and magnesium oxides, including hydroxychlorides, in methanol[12,13,14]. In the present study, samples of this feed were leached in ultra pure methanol and the leaching residues were filtered and dried at about 100 °C; a temperature not high enough to change the composition of isolated oxide but high enough to remove the methanol. The isolated material was characterized with a novel speciation method[14] and identified to be only $Mg_2(OH)_3Cl.2H_2O$. The XRD spectrum for the dried leach residue is shown in Figure 56. It is noteworthy that MgO was not found in that feed material since MgO has commonly been assumed to be present in these feeds.

In the absence of thermodynamic data for $Mg_2(OH)_3Cl.nH_2O$[15], the present authors suggest that its decomposition may occur as follows based on our observations of the digestion behavior of commercial feeds in commercial magnesium production electrolytes[16].

$$Mg_2(OH)_3Cl.nH_2O_{(s)} = 2MgO_{(s)} + HCl_{(g)} + (n+1)H_2O_{(g)} \qquad (74)$$

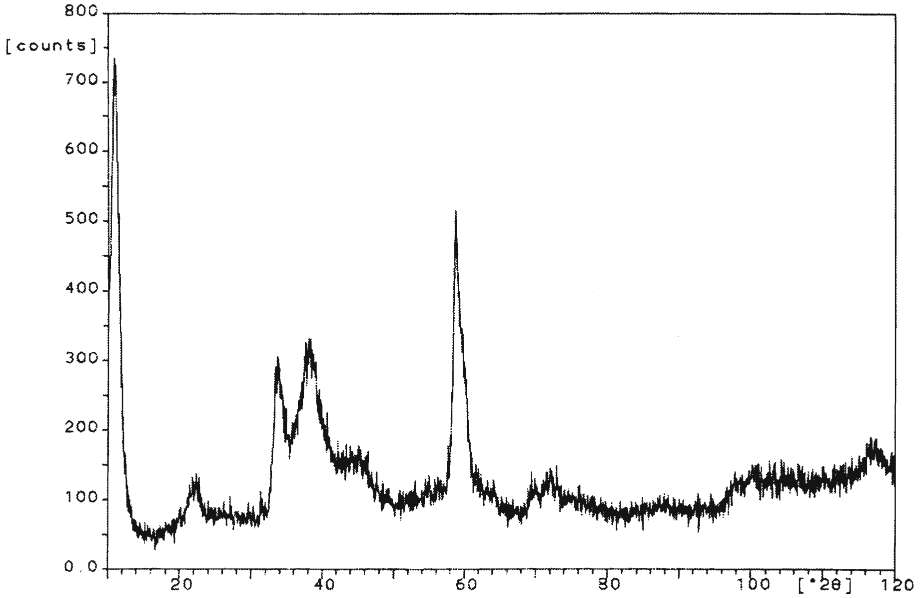

Figure 56: XRD Spectrum of Leach Residue Identified as $Mg_2(OH)_3Cl.2H_2O$ by the Authors' Technique.

11.3: Thermal Gravimetric Analysis

The TGA tests on $Mg_2(OH)_3Cl.2H_2O$ were performed with a 'Cahn thermo 700 TGA' machine into which 0.114 g of the isolated sample were charged in a high alumina crucible, after which the furnace was purged with ultra-pure, dry helium. The sample was heated to 600 °C at a heating rate of 15 °C / min, kept at 600 °C for 30 min and allowed to cool by natural convection in the furnace. The mass change curve of the sample is presented in Figure 57. It can be seen that the thermal decomposition underwent one intermediate stage at about 108 °C. The fraction of initial mass loss indicated that the sample initially contained about two molecules of water. After losing its crystalline water, the sample subsequently converting to MgO, as identified by XRD analysis of the final product, once the temperature was increased over 398 °C. A SEM image of this poorly crystalline magnesium hydroxychloride is presented in Figure 58.

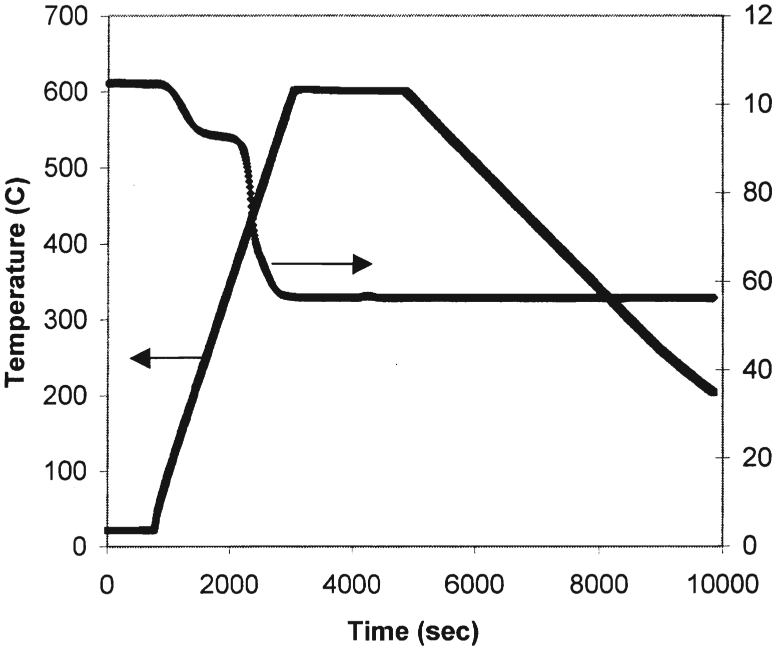

Figure 57: TGA Results for $Mg_2(OH)_3Cl.2H_2O$ Decomposition.

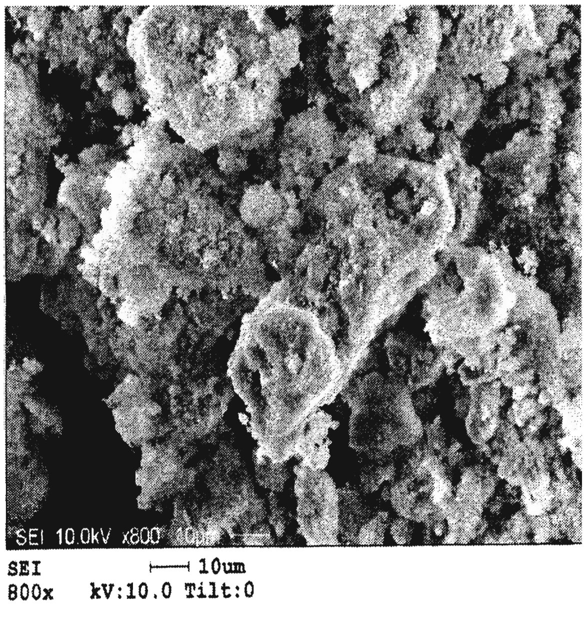

Figure 58: SEM Image of Leach Residue Identified as $Mg_2(OH)_3Cl.2H_2O$.

11.4: Isothermal Decomposition of $Mg_2(OH)_3Cl$

Experiments were designed to study the isothermal decomposition of $Mg_2(OH)_3Cl$ at 400, 450, and 500 °C. In these experiments, 6 samples at a time of $Mg_2(OH)_3Cl$ (1 g each), held in high alumina crucibles, were placed into a furnace kept at the desired temperature. The time required to heat the sample to the furnace temperature was found to be about 10 seconds. The instant when the samples reached the desired temperature was considered to be the beginning of the decomposition process. Samples were removed one by one from the furnace at regular time intervals and were canned, quickly transferred to a dry glove box. Thereafter their masses were precisely measured and their structure analyzed by XRD.

XRD analysis revealed that the $Mg_2(OH)_3Cl$ sample gradually decomposed into MgO. The XRD spectra of samples processed at 400 °C for different times is shown in Figure 52. It can be seen that the characteristic peak of $Mg_2(OH)_3Cl$ gradually diminished as processing time increased. At 30 minutes, only the MgO peaks remained.

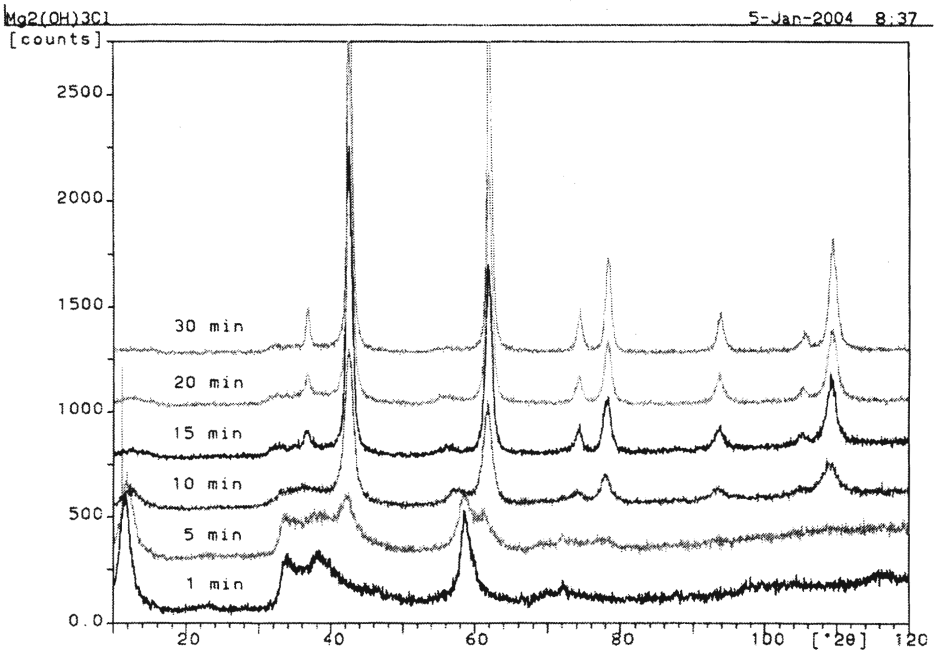

Figure 59: XRD Spectra of $Mg_2(OH)_3Cl$ Decomposition Products vs. Time at 400 °C.

The mass of the sample at any time in the experiment was the sum of the mass of $Mg_2(OH)_3Cl$ remaining in the sample and the mass of MgO produced by the decomposition reaction. Assuming the decomposition reaction occurred according to

Reaction 74, the percentage of $Mg_2(OH)_3Cl$ remaining in the sample with respect to its original mass was calculated from the mass loss of the sample. A semi-logarithmic plot of the change in weight percent of $Mg_2(OH)_3Cl$ sample remaining with time is presented in Figure 60. Each data point represents the average of three repeated measurements. As can be seen, the decomposition of $Mg_2(OH)_3Cl$ consisted of two stages. The linearity of the data indicates that the kinetics of both stages were first order with respect to the weight percent of the $Mg_2(OH)_3Cl$ remaining in the sample. However, the rate of decomposition is different in these two stages.

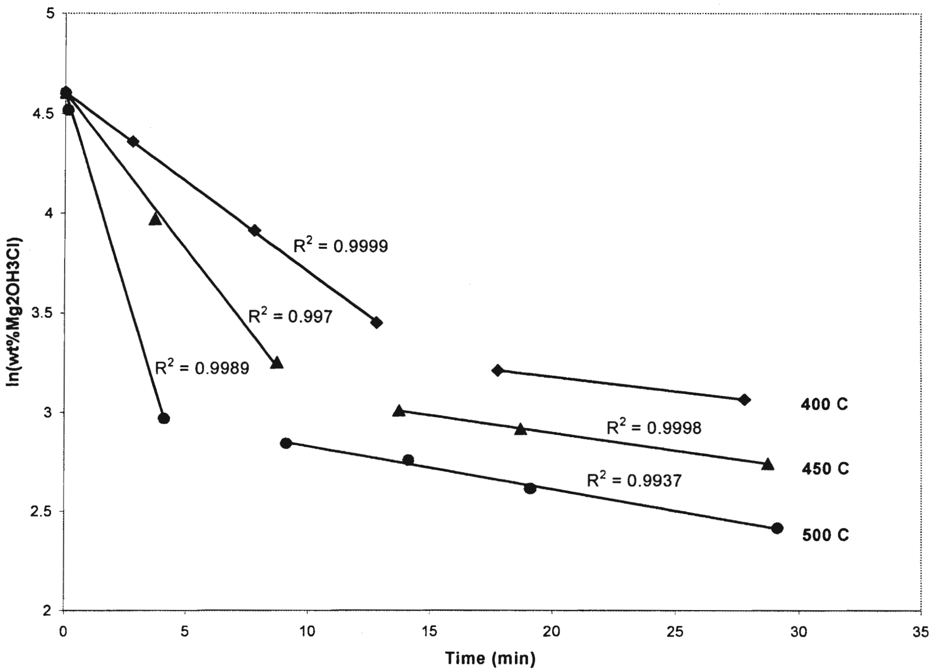

Figure 60: Kinetics of $Mg_2(OH)_3Cl$ Thermal Decomposition.

Figure 61 presents an “Arrhenius plot” of the kinetics of decomposition of both stages, i.e., a plot of the semi-logarithm of the decomposition rate constants, k, which were the slopes of the linear regression lines in Figure 60, vs. reciprocal temperature. From linear regression of the three points, the decomposition rate constant, k, of the two stages of decomposition was found to have the following dependence on temperature:

$$Stage 1: \quad \ln k = -7687\frac{1}{T} + 8.9 \qquad (75)$$

$$Stage\,2: \quad \ln k = -2119\frac{1}{T} - 1.1 \tag{76}$$

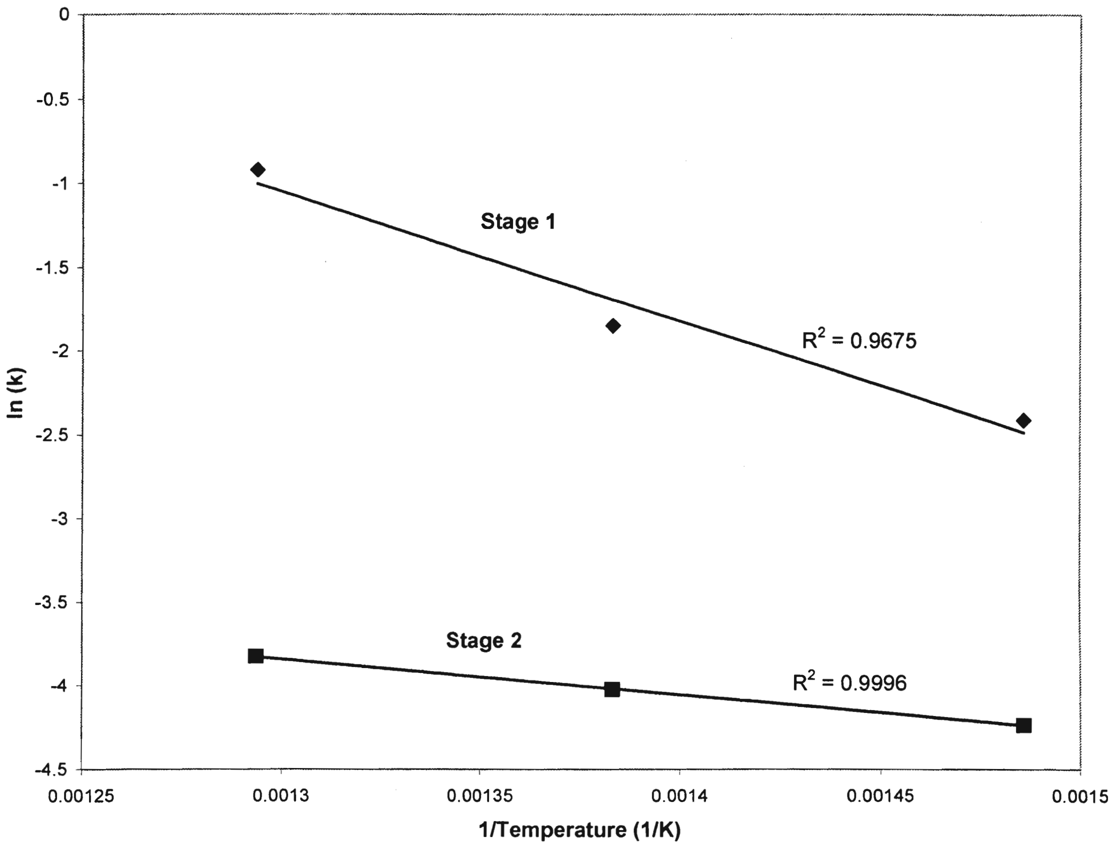

Figure 61: Arrhenius Plot of Thermal Decomposition of $Mg_2(OH)_3Cl$.

Detailed analysis of the first order kinetic relationship revealed that the kinetics of the decomposition of $Mg_2(OH)_3Cl$ was controlled by the rate of removal of a gaseous product released during the course of the decomposition (see Appendix A). Moreover, the coefficient of the first term in the temperature dependence of the decomposition rate constant of $Mg_2(OH)_3Cl$ in stage 1 was found very similar to the one obtained in the study of the thermal decomposition of the MgOHCl (i.e. –7868)[17]. This observation suggested that the gas released in stage 1 of decomposition of $Mg_2(OH)_3Cl$ is same as that released in the decomposition of MgOHCl, which was HCl gas. As can be seen in reaction 74, the two gases released in the decomposition of $Mg_2(OH)_3Cl$ are HCl and H_2O. Therefore, it is proposed that the change in decomposition rate observed is the result of H_2O being released in stage 2 of the decomposition of $Mg_2(OH)_3Cl$ instead of HCl gas.

A change in the gaseous product released due the course of decomposition of $Mg_2(OH)_3Cl$ can be explained by considering $Mg_2(OH)_3Cl$ as a mixture of $Mg(OH)_2$ and $MgCl_2$. When $Mg_2(OH)_3Cl$ is considered as a mixture of $Mg(OH)_2$ and $MgCl_2$, the molar ratio of $Mg(OH)_2$ to $MgCl_2$ is 3:1. As decomposition of $Mg(OH)_2$ occurs, H_2O is released. The H_2O released reacts with $MgCl_2$ to produce HCl gas. Therefore, the gas released in the stage 1 is HCl gas. Due to the $Mg(OH)_2$ being in excess, the $MgCl_2$ can be completely reacted by the H_2O released in the decomposition of $Mg(OH)_2$. Once all $MgCl_2$ in the sample is consumed, the gaseous product released in the decomposition is H_2O, which is corresponds to the stage 2 observed in the experiment. Such behavior was not observed in the decomposition of MgOHCl because the molar ratio of $Mg(OH)_2$ to $MgCl_2$ in MgOHCl is 1:1, i.e., $MgCl_2$ is always present until the sample is fully decomposed. Therefore, the only gaseous species released in the decomposition of MgOHCl was HCl gas.

11.5: Conclusions

The kinetics of thermal decomposition of $Mg_2(OH)_3Cl.2H_2O$ was studied. It was found that the decomposition of $Mg_2(OH)_3Cl.2H_2O$ commenced at about 108 °C with the loss of crystalline water followed by the decomposition of $Mg_2(OH)_3Cl$ into MgO, H_2O and HCl at temperatures above 300 °C. The decomposition of $Mg_2(OH)_3Cl$ consisted of two stages. In the first stage, HCl gas was released and in the second stage H_2O was produced. Kinetic measurements revealed that both stages were first order with respect to the amount of $Mg_2(OH)_3Cl$ remaining, which suggested that the decomposition kinetics was controlled by the rate of removal of the released gaseous product. The change in decomposition rate was due to the change in gaseous species released in the course of decomposition.

11.6: Acknowledgement

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2452600-00 and Noranda Technology Center Magnesium Group for their enthusiasm and support of student learning.

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11.8: Appendix A

The differential form of the decomposition rate of a sample of particles of $Mg_2(OH)_3Cl$ can be written as follows.

$$\frac{d}{dt}\left(wt\%\,Mg_2(OH)_3Cl\right)=k\left(wt\%\,Mg_2(OH)_3Cl\right) \qquad (77)$$

The above equation can be reduced to:

$$\frac{\rho N}{M_i}\frac{d}{dt}(V_t)=k\left(\frac{\rho N}{M_i}\right)(V_t) \qquad (78)$$

Where ρ = density of $Mg_2(OH)_3Cl$, M_i = initial mass, V_t = volume of $Mg_2(OH)_3Cl$ particles at time t and N = number of particles.

Assuming a $Mg_2(OH)_3Cl$ particle is spherical, the equation can be further reduced to:

$$\frac{d}{dt}(r)=k\left(\frac{r}{3}\right) \qquad (79)$$

where r = radius of the particle at time t. As can be seen, the rate of shrinkage of the particle is related to r/3, which is equivalent to the volume to surface ratio of a spherical particle. In other words, the rate of decomposition of the $Mg_2(OH)_3Cl$ is determined by the surface available. Furthermore, in the study of the decomposition kinetics of MgOHCl, a similar kinetic expression was obtained.

It was also observed that purging of the gas atmosphere with inert gas doubled the decomposition rate of MgOHCl. Based on these observations, it was concluded that the kinetics of the decomposition of magnesium hydroxychloride was controlled by the rate of removal of the gaseous compounds being produced according to the following reaction.

$$MgOHCl_{(s)} = MgO_{(S)} + HCl_{(g)} \qquad (80)$$

Chapter 12: Conclusions, Original Contributions and Future Work

12.1: Conclusions

12.1.1: It was concluded that the kinetics of mass transfer of water vapour away from the dehydration site played a major role in the formation of magnesium hydroxychloride during dehydration of magnesium chloride hexahydrate. Such conclusion was based on the finding that the hydrolysis of magnesium chloride that was formed by the dehydration of magnesium chloride hexahydrate was a fast process in comparison to the time required for dehydration. Consequently, there was opportunity for hydrolysis to occur before dehydration was complete due to the time required for transport of the evolved waters of crystallization away from the magnesium chloride produced upon liberation of the waters of crystallization.

12.1.2: It was concluded that the mechanism of magnesium oxide and magnesium hydroxychloride formation during the dehydration of magnesium chloride hydrates was more complex than was indicated in the literature. In particular, it was found that there was an initial, very rapid 'rearrangement' of the Mg, Cl, H and O atoms during the dehydration to produce a poorly crystalline magnesium hydroxychloride phase. It was also found that that this '*primary*' magnesium hydroxychloride formation occurs to some extent at all temperatures.

12.1.3: It was concluded that the magnesium hydroxychlorides produced during dehydration have different thermal stabilities. Clearly, this different behavior of the magnesium hydroxychlorides, the characterizations of which were previously impossible, adds yet another constraint that needs to be taken into consideration in the design of industrial processes based on the industry standard technique of trying to prevent hydrolysis through use of sufficiently high $pHCl/pH_2O$ in the gas phase or by sufficiently suppressing the $MgCl_2$ activity in the product.

12.2: Contributions to Original Knowledge

The research accomplished the followings:

12.2.1: Magnesium Oxides Speciation Technique

A novel and accurate method was developed to determine the composition and quantities of magnesium '*oxides*' present in the feeds or fused salt melts used for the commercial electrolytic magnesium production process regardless of the nature of the oxide species present. The method overcomes the limitations of previous techniques, especially with regard to considering different forms of hydroxychlorides in the sample and the possible presence of other impurities.

12.2.2: Dehydration of $MgCl_2.6H_2O$

The composition and extent of formation of oxides during thermal dehydration of $MgCl_2.6H_2O$ (bischofite) upon holding at temperature under an uncontrolled atmosphere were found to be significantly influenced by the dehydration temperature. The oxide formed was found to be poorly crystalline MgOHCl for all temperatures other than 600 °C where it also contained some MgO. Upon holding at temperature, it was found that the oxide formation occurred gradually at temperatures up to 400 °C and the amount of the oxides formed from the ongoing hydrolysis increased with holding time. A significant increase in oxide formation rate was observed when the dehydration temperature was increased from 400 °C to 500 °C.

12.2.3: MgOHCl Preparation and Characterization

- High purity crystalline MgOHCl was successfully prepared via controlled dehydration of $MgCl_2.6H_2O$.
- The solubility of MgOHCl in methanol was measured to be 1.26×10^{-3} g/100 ml and its characteristic infrared spectrum absorption peak was identified at 3550 cm^{-1}.

12.2.4: MgOHCl Thermal Decomposition Kinetics

The thermal decomposition of MgOHCl under an uncontrolled atmosphere was found to be a first order kinetic process. Moreover, the removal of the produced HCl gas was found an important factor governing the rate of the decomposition. The decomposition rate constant was related to temperature by the follow relationship:

$$\ln k = -7868\frac{1}{T} + 7.6$$

12.2.5: $Mg_2(OH)_3Cl.2H_2O$ Thermal Decomposition Kinetics

- $Mg_2(OH)_3Cl.2H_2O$ was isolated from (i) the feed material of a commercial electrolytic magnesium production process and (ii) from non-equilibrium products of dehydration of $MgCl_2.6H_2O$ under an uncontrolled atmosphere.
- The thermal decomposition of $Mg_2(OH)_3Cl.2H_2O$ under uncontrolled atmosphere was found to be consist of two stages. Decomposition in each stage found to be a first order kinetic and the rate of removal of the released gaseous products was proved to be an important factor governing the rate of the decomposition. The decomposition rate constant, k, of the two stages of decomposition was found to have the following dependence on temperature:

$$\mathit{Stage}\ 1: \quad \ln k = -7687\frac{1}{T} + 8.9$$

$$\mathit{Stage}\ 2: \quad \ln k = -2119\frac{1}{T} - 1.1$$

12.3: Recommendation for Future Work

12.3.1: The research in this thesis focused on the thermal dehydration of $MgCl_2.6H_2O$ under an uncontrolled atmosphere. It would be of interest to study dehydration of magnesium chloride hydrates under controlled atmospheres with varying P_{HCl}/P_{H2O}.

12.3.2: Measurement of the thermochemical properties of $Mg_2(OH)_3Cl.2H_2O$, would allow the development of a better understanding of the formation of these oxides during the dehydration of magnesium chloride hydrates.