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A thermochemical analysis of the production of anhydrous $MgCl_2$

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Abstract

The electrolytic production of magnesium requires high-purity, anhydrous magnesium chloride which has a high affinity for water and is found in nature as a plurality of hydrates ($MgCl_2 \cdot nH_2O$, $n = 1, 2, 4, 6, 8, 12$). Their dehydration is nontrivial and can be accompanied by hydrolysis leading to the production of undesirable oxycompounds of magnesium. Through an analysis of the relevant thermochemistry this paper indicates how to prevent hydrolysis and make electrolytic-grade, anhydrous $MgCl_2$.

Keywords: Magnesium; Hydrolysis; Dehydration; Thermochemistry

1. Introduction

With a density of 1.74 g/cm^3 magnesium is 4.5 times lighter than steel and 1.6 times lighter than aluminum [1]. The mechanical properties of magnesium castings make them competitive with aluminum castings. When hot worked, magnesium is the easiest to deep draw of the common metals and requires the least energy to machine. It has superior damping capacity owing to its high specific stiffness.

The expectation of increased utilization of magnesium in automotive applications has stimulated renewed commercial interest in this metal [2]. In fact, at this moment, the combined tonnage of announced greenfield projects exceeds total global production capacity [3]. By far the dominant extraction technology is molten salt electrolysis of magnesium chloride to produce liquid magnesium and chlorine gas. While electrolytic reduction appears straightforward, the process cannot be sustained without the availability of high-purity feed, i.e., anhydrous magnesium chloride. Owing to its high affinity for water as evidenced by the large number of hydrates ($MgCl_2 \cdot nH_2O$, $n = 1, 2, 4, 6, 8, 12$), the production of anhydrous magnesium chloride is not trivial. In an effort to help workers in the field avoid the pitfalls, the present paper presents the relevant thermochemistry.

2. Background

A cubic kilometer of seawater contains approximately a million tones of magnesium, more than has ever been produced in one year by all the magnesium plants in the world. Furthermore, seawater contains only 3.7% of the total magnesium present in the earth's crust. Clearly, magnesium resources are ubiquitous and virtually inexhaustible.

Due to its reactivity, magnesium is never found in nature in its free state but rather in compounds: *as chlorides* ($MgCl_2 \cdot 12H_2O$) in seawater (0.25–0.55%), in underground brines (up to 20%), and in salt deposits such as carnallite ($MgCl_2 \cdot KCl \cdot 6H_2O$), and *as carbonates* in the ores dolomite ($MgCO_3 \cdot CaCO_3$) and magnesite ($MgCO_3$). Less important are the surface minerals, kieserite ($MgSO_4 \cdot H_2O$), kainite ($MgSO_4 \cdot KCl \cdot 3H_2O$) and langbeinite ($2MgSO_4 \cdot K_2SO_4$). Finally, magnesium can be found in certain waste streams in concentrations high enough to warrant commercial interest. For example, asbestos tailings contain magnesium in the form of serpentine ($Mg_3Si_2O_5(OH)_4$) [4].

In the electrolytic production of magnesium, magnesium chloride is dissolved in a solvent consisting of a multicomponent solution of alkali and alkaline-earth chlorides. The action of electric current drives faradaic processes that produce liquid magnesium and chlorine gas through the decomposition of magnesium chloride. The temperature of operation is typically between 700°C and 750°C. Magnesium droplets form on the steel cathode, and chlorine bubbles form on the carbon an-

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ode. Both cell products rise to the surface of the electrolyte where they are collected. As these reactions proceed the electrolyte is depleted of magnesium chloride, which must be periodically added to the melt. While the stoichiometry of the magnesium chloride sets the molar ratio of cell products at 2:1 chlorine:magnesium, on a volumetric basis the ratio is 5800:1! One might argue that the electrolysis of magnesium chloride produces chlorine, and magnesium is the by-product.

Magnesium metal was first produced electrolytically by Faraday in 1833. Modern electrolytic cell technology emerged in Germany in the late 19th century. Today there are several variants [1] but all can be traced back to the I.G. Farben cell which uses anhydrous $MgCl_2$ as feed. In the 1930s, Dow developed a cell designed to accept partially hydrated $MgCl_2$ as feed. Since 1998, all electrolytic magnesium is produced by anhydrous technology.

Although it is not the only harmful impurity present in $MgCl_2$, water is an unwanted component of the cell feed for many reasons:

1. At electrolysis temperatures hydrolysis occurs, i.e., the water of hydration in $MgCl_2 \cdot nH_2O$ does not remain intact, but instead dissociates. This generates highly reactive hydrogen and oxygen species which attack $MgCl_2$ to produce hydrogen chloride gas and various oxycompounds of magnesium. Hydrogen chloride attacks the equipment and renders the chlorine produced at the anode unmarketable. Some oxycompounds are insoluble in the electrolyte and cause sludging.
2. Soluble oxycompounds can participate in parasitic electrochemical reactions on the carbon anode consuming it in the process. This attendant dimensional instability means suboptimal cell operation, e.g., undesirable changes in joule heating rates and electrolyte circulation patterns.
3. Soluble oxycompounds can react with nascent magnesium droplets forming a surface film that prevents their coalescence.

3. The thermochemistry of the hydrates of $MgCl_2$

Magnesium chloride is very hygroscopic. As shown in Fig. 1, water can become chemically bound to form a series of hydrate compounds ($MgCl_2 \cdot nH_2O$, $n = 1, 2, 4, 6, 8, 12$) [5]. It should be noted that $MgCl_2$ and H_2O, the two terminal components of the phase diagram depicted in Fig. 1, are only two of the stable compounds that form in the Mg–Cl_2–O_2–H_2 system. In the event of hydrolysis, one can expect to find magnesium bound not only to chlorine, but also to oxygen and hydrogen, e.g., MgOHCl (see Eq. (4)).

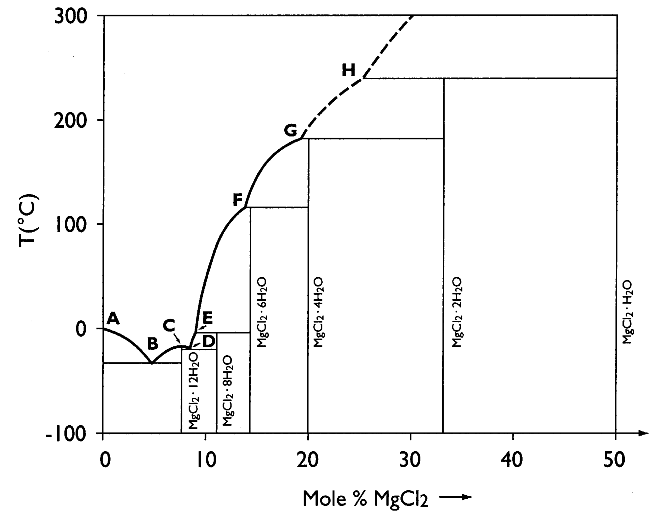

Fig. 1. Phase diagram of the magnesium chloride – water system (schematic).

At room temperature the most fully hydrated form of magnesium chloride is the hexahydrate, $MgCl_2 \cdot 6H_2O$. Its dehydration proceeds by the following reaction:

$$MgCl_2 \cdot 6H_2O_{(s)} = MgCl_2 \cdot 4H_2O_{(s)} + 2H_2O_{(v)} \tag{1}$$

over the temperature range 298–390 K, where the solid hexahydrate is stable.

The dehydration of $MgCl_2 \cdot 4H_2O$ occurs by conversion to the dihydrate by the reaction:

$$MgCl_2 \cdot 4H_2O_{(s)} = MgCl_2 \cdot 2H_2O_{(s)} + 2H_2O_{(v)} \tag{2}$$

Dehydration of the solid dihydrate by conversion to the monohydrate occurs by the reaction:

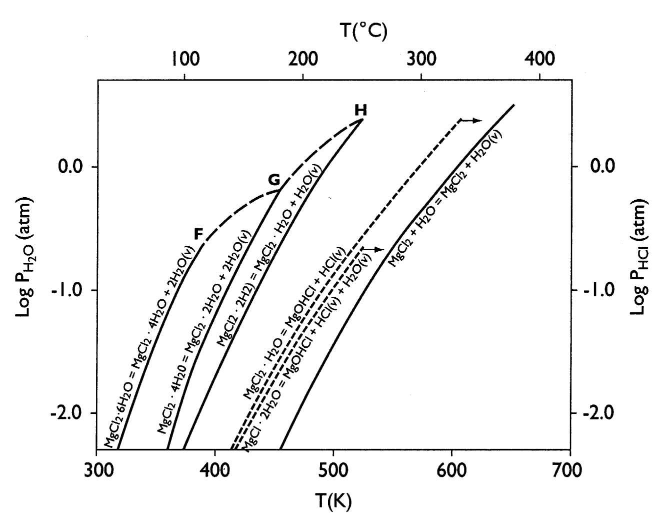

Fig. 2. Vapor pressures of H_2O and HCl over the hydrates of magnesium chloride.

[1] The differences between the I.G. Farben cell and the VAMI cell can be attributed to the Russian practice of producing anhydrous feed from carnallite. VAMI is the acronym for the All-Union Aluminum and Magnesium Institute.

$$MgCl_2 \cdot H_2O_{(s)} = MgCl_2 \cdot H_2O_{(s)} + H_2O_{(v)} \quad (3)$$

over the temperature range where the dihydrate is stable.

It should be noted that dehydration of the dihydrate can also proceed by hydrolysis:

$$MgCl_2 \cdot 2H_2O_{(s)} = MgOHCl_{(s)} + HCl_{(g)} + H_2O_{(v)} \quad (4)$$

Reaction (4) is inhibited by the greater vapor pressure of water generated by reaction (3), which occurs simultaneously. Hydrolysis can be prevented by the use of HCl according to Le Chatelier's Principle provided that the partial pressure of HCl exceeds the value calculated by Eq. (4). Fig. 2 plots the temperature dependence of this threshold P_{HCl}.

The final stage in dehydrating magnesium chloride is to remove the last water of crystallization from the solid monohydrate by the reaction:

$$MgCl_2 \cdot H_2O_{(s)} = MgCl_{2(s)} + H_2O_{(v)} \quad (5)$$

The hydrolysis reaction corresponding to Eq. (5) is

$$MgCl_2 \cdot H_2O_{(s)} = MgOHCl_{(s)} + HCl_{(g)} \quad (6)$$

Fig. 2 shows variation in the partial pressure of HCl with temperature for Eq. (6).

Reactions (5) and (6) can be combined to express the hydrolysis of $MgCl_2$ as

$$MgCl_{2(s)} + H_2O_{(v)} = MgOHCl_{(s)} + HCl_{(g)} \quad (7)$$

which allows a calculation of the minimum ratio of P_{HCl}/P_{H_2O} to avert hydrolysis. As shown in Fig. 2, the vapor pressure of HCl under these circumstances is considerably higher than that of H_2O. This suggests that unless precautions are taken, the hydrolysis reaction (7) will proceed in preference to the dehydration reaction (5). Alternatively, hydrolysis can be averted when the applied partial pressure of HCl exceeds that shown in Fig. 2 for reaction (7).

In the light of the above reactions (1)–(7), the dehydration of $MgCl_2 \cdot 6H_2O$ will produce anhydrous $MgCl_2$ as long as the final step, reaction (5), is performed under a blanket of HCl at a partial pressure given in Fig. 2. It has been reported [6] that the entire dehydration sequence starting from hexahydrate is conducted under HCl. The thermodynamic analysis presented in [5] shows that up to reaction (4) it is not necessary to use HCl provided that no liquid phase is present.

In an attempt to improve the kinetics of the process, workers may be tempted to conduct dehydration at elevated temperatures where either the hydrates or the product $MgCl_2$ are present as liquid. Under these circumstances, the value of the partial pressure of HCl capable of preventing hydrolysis is substantially higher than that shown in Fig. 2. Unfortunately, the thermodynamic properties of multicomponent chloride melts containing dissolved oxycompounds have not been measured. Thus, absent these data, accurate determination of the P_{HCl}/P_{H_2O} ratio is not possible. Just the same, it is easy to appreciate that if dehydration of the monohydrate occurs under conditions that yield molten $MgCl_2$ containing a small amount of dissolved MgOHCl such that $a_{MgOHCl}/a_{MgCl_2} = 0.01$, then the ratio of P_{HCl}/P_{H_2O} necessary to chlorinate the impurity is greater by a factor of 100 compared to the situation in which there is no liquid phase. Thus, dehydration at higher temperatures requires attendant changes in process chemistry. By way of example, Magnola employs a so-called superchlorinator [7].

A final note on the dehydration of magnesium chloride concerns the stability of the oxychloride, MgOHCl, which can decompose according to the reaction

$$MgOHCl_{(s)} = MgO_{(s)} + HCl_{(g)} \quad (8)$$

The decomposition temperature of MgOHCl, i.e., the temperature at which the pressure of HCl reaches 1 atm, is calculated [5] to be 828 K. Above this temperature the oxychloride formed during dehydration will be converted entirely to MgO according to reaction (8). Solubilities of the various oxidation products have been determined [8]. Hydroxychloride formation and its effect on melt chemistry is probably more complex than it appears, as there many hydroxychloride species reported in literature. To complicate further the issue, some of these hydroxychlorides are reported to have hydrates. Due to the complexity of the system some authors refer to the retained water as "occluded" water. Table 1 shows the formulae of all the hydroxychlorides and their hydrates for which powder diffraction files (PDF) have been reported in the cards of the Joint Committee on Powder Diffraction Standards (JCPDS). Although the plethora of the proposed hydroxychlorides may cast doubt on their existence, nevertheless, it testifies to the complexity of the $Mg–Cl_2–O_2–H_2$ system.

In industrial practice, kinetics, which do not appear to have been extensively studied in this system, play a major role. Indeed, spray drying under optimum conditions can produce material with 1% H_2O and 1% MgO, although normal practice gives 2–5% H_2O and 2–5% MgO.

To avoid some of the problems presented by the dehydration of hydrated magnesium chloride, other chemistries for cell feed preparation have been investigated. Some of these, particularly those involving ammonium chloride salts, have been tested at the pilot plant level. These include dehydration of double salts and chlorination of magnesium oxide.

Magnesium chloride and potassium chloride form a hydrated double salt called carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$. Since KCl is also a major component of the electrolyte, one option in cell feed preparation is to produce anhydrous $KCl \cdot MgCl_2$ directly from carnallite. Proponents of the use of carnallite have argued that it is easier to dehydrate than $MgCl_2 \cdot nH_2O$. Closer examination shows this not to be the case.

The dehydration of carnallite proceeds according to the reactions

$$KCl \cdot MgCl_2 \cdot 6H_2O_{(s)} = KCl \cdot MgCl_2 \cdot 2H_2O_{(s)} + 4H_2O_{(v)} \quad (9)$$

and

$$KCl \cdot MgCl_2 \cdot 2H_2O_{(s)} = KCl \cdot MgCl_{2(s)} + 2H_2O_{(v)} \quad (10)$$

accompanied to a certain extent by hydrolysis according to reaction (7). Although it appears that dehydration of carnallite is similar to that of magnesium chloride, there is a significant difference between the two. Any hydroxychloride generated during the dehydration of carnallite forms a solid solution with it. Upon melting, the hydroxychloride dissociates according to

$$MgOHCl = MgOH^+ + Cl^- \quad (11)$$

thereby generating cationic impurities, which can interfere with the electrochemical reduction of magnesium in the electrolytic cell. To prevent hydrolysis a blanket of dry hydrogen chloride gas should be present. Thus, the process is in practice as complicated as the dehydration of magnesium chloride and appears to offer no advantages over the latter. Furthermore, long-term cell feeding with dehydrated carnallite eventually requires either that pure $MgCl_2$ make-up be added or that supporting electrolyte be withdrawn to keep its composition within limits.

Another double salt is ammonium carnallite, $NH_4Cl \cdot MgCl_2 \cdot 6H_2O$. Dehydration occurs by the following steps:

$$NH_4Cl \cdot MgCl_2 \cdot 6H_2O_{(s)} \xrightarrow{373\ K} NH_4Cl \cdot MgCl_2 \cdot 4H_2O_{(s)} + 2H_2O_{(v)} \quad (12)$$

$$NH_4Cl \cdot MgCl_2 \cdot 4H_2O_{(s)} \xrightarrow{413\ K} NH_4Cl \cdot MgCl_2 \cdot 2H_2O_{(s)} + 2H_2O_{(v)} \quad (13)$$

$$NH_4Cl \cdot MgCl_2 \cdot 2H_2O_{(s)} \xrightarrow{433\ K} NH_4Cl \cdot MgCl_{2(s)} + 2\ H_2O_{(v)} \quad (14)$$

$$NH_4Cl \cdot MgCl_{2(s)} \xrightarrow{509\ K} NH_4Cl_{(v)} + MgCl_{2(s)} \quad (15)$$

Heating ammonium carnallite to 450 K will result in dehydration according to reactions (12)–(14). In a second step, reaction (15) is carried out by maintaining a temperature of 573 K. The last step should be conducted upon complete removal of the water of crystallization, otherwise hydrolysis will occur via reaction (11). The patent literature [9] describes several variations of this method of dehydration. Dehydration of ammonium chloride in an ammonia atmosphere or in the presence of an organic phase is also described [10].

Recently dehydration of ammonium double salts, which has its merits, has been tried at the pilot plant scale. It seems that the higher energy consumption may offset the advantages. Carnallite dehydration has been used on an industrial scale in Russia and recently in Israel. Ammonium carnallite dehydration has been practiced at the laboratory scale by the authors of the present paper. The product anhydrous $MgCl_2$ was then sublimed in an inert atmosphere containing $SOCl_2$ to give a highly purified material for spectral studies [11,12].

Difficulties in the dehydration of $MgCl_2 \cdot 6H_2O$ led to the development of processes for the direct chlorination of magnesium oxide. Magnesium oxide can be produced by calcination (~1000°C) of either magnesite or magnesium hydroxide precipitated by mixing seawater with dolime.

Table 1
PDF for reported hydroxides of magnesium and their hydrates

Formula	Name	File number	Year
MgClOH	Magnesium chloride hydroxide	24–726	1970
$Mg_2(OH)_3Cl$	β-magnesium chloride hydroxide	12–410	1954
MgOHCl	Magnesium chloride hydroxide	3–100	1944
Mg(OH)Cl	Magnesium chloride hydroxide	11–328	1953
$Mg_2Cl(OH)_3$	Magnesium chloride hydroxide	12–120	1958
$Mg_2Cl(OH)_3 \cdot 4H_2O$	Magnesium chloride hydroxide hydrate	36–388	1982
$Mg_3Cl_2(OH)_4 \cdot 2H_2O$	Magnesium chloride hydroxide hydrate	12–133	1958
$Mg_{10}Cl_2(OH)_{18} \cdot 5H_2O$	Magnesium chloride hydroxide hydrate	12–123	1958
$Mg_3Cl(OH)_5 \cdot 4H_2O$	Magnesium chloride hydroxide hydrate	12–122	1958
$Mg_3(OH)_5Cl \cdot 4H_2O$	Magnesium chloride hydroxide hydrate	7–420	1949
$Mg_2(OH)_3Cl \cdot 2H_2O$	Magnesium chloride hydroxide hydrate	7–419	
$Mg_3(OH)_5Cl \cdot 3H_2O$	Magnesium chloride hydroxide hydrate	7–416	
$Mg_2(OH)_3Cl \cdot 4H_2O$	Magnesium chloride hydroxide hydrate	7–412	
$Mg_{10}(OH)_{18}Cl \cdot 5H_2O$	Magnesium chloride hydroxide hydrate	7–409	
$Mg_2(OH)_3Cl \cdot 3H_2O$	Magnesium chloride hydroxide hydrate	7–403	

The chlorination of magnesium oxide can be represented by the reaction

$$MgO_{(s)} + Cl_{2(g)} = MgCl_{2(s\ or\ l)} + 1/2O_{2(g)} \quad (16)$$

where $MgCl_2$ is solid below 987 K and molten above this temperature. The thermodynamics of the process are explained in [5,8].

At 1300 K, which is the temperature at which industrial chlorinators operate, the oxygen content of the gas should be kept below 1.4 mol% at 1 atm total pressure. Failure to do so will result in oxidation of $MgCl_2$, i.e., reaction (16) proceeds to the left. In industrial practice, to achieve an acceptable rate of chlorination, the pressure of oxygen will be allowed to increase above the equilibrium value. This necessitates the use of a suitable reducing agent such as carbon to act as an oxygen sink.

Carbochlorination occurs by the reaction

$$MgO_{(s)} + Cl_{2(g)} + C_{(s)} = MgCl_{2(l)} + CO_{(g)} \quad (17)$$

The reaction products are very stable. Thus, when a stream of chlorine gas passes through a mixture of MgO and C maintained at a constant temperature of 1300 K the gas phase will consist almost entirely of CO provided that equilibrium is achieved. On the other hand, since most industrial chlorination reactors have been designed to consume a minimum amount of reagent (carbon) and do not operate isothermally, the gas phase tends to be a mixture of CO, CO_2, Cl_2 and volatile chlorides.

Carbon monoxide itself, however, is also a reducing agent initiating a strongly exothermic reaction:

$$MgO_{(s)} + Cl_{2(g)} + 2CO_{(g)} = MgCl_{2(l)} + CO_{2(g)} \quad (18)$$

Proper control of the temperature of the chlorination furnace is essential for its successful operation.

In a patent [13] the carbochlorination of magnesium carbonate (instead of magnesium oxide) by chlorine and carbon monoxide gases in a packed bed reactor to produce anhydrous molten magnesium chloride is described. The reaction is

$$MgCO_{3(s)} + CO_{(g)} + Cl_{2(g)} = MgCl_{2(l)} + 2CO_{2(g)} \quad (19)$$

Carbon dioxide is removed from the top of the reactor, and anhydrous molten magnesium chloride is withdrawn below the packed bed. The energy requirements are claimed to be low, and the kinetics favorable. The one attempt to commercialize the process was unsuccessful.

A detailed description of chlorination technology as it applies to MgO in general has been given elsewhere [14]. Magnesium oxide mixed with carbon and magnesium chloride acting as a binder is formed into pellets, which are dried and fed into the top of an electrically heated shaft furnace while chlorine enters at the bottom. In a continuous operation molten magnesium chloride is tapped periodically into crucibles and fed to the electrolysis cells.

New environmental restrictions have forced re-examination of the carbochlorination process for two main reasons. First, under certain conditions environmentally unacceptable polychlorinated hydrocarbons may be produced [15] and second, the chlorination furnaces are not easy to control. For improved efficiency it is necessary to optimize the charge with respect to particle size distribution, particle porosity, activity of the reducing agent, i.e., grade of carbon, as well as with respect to the concentrations of certain impurities.

While the focus of this article has been the dehydration of various forms of $MgCl_2 \cdot nH_2O$, the production of electrolytic-grade, anhydrous $MgCl_2$, implies material free of impurities. Impurities not only contaminate the metal but also interfere with the operation of the electrolytic cells and affect their productivity. This is due to the fact that, even at trace concentration levels, impurities can adversely change the physical properties of the electrolyte.

Sources of $MgCl_2$ can also contain oxides and sulfates, as well as boron. Table 2 shows the maximum permissible levels of commonly occurring impurities.

When cell feed is produced by dehydration of hydrated magnesium chloride concentrated from seawater or brines, sulfates are removed as calcium sulfate. It was found [5] that the solubility of $CaSO_4$ decreases as $MgCl_2$ content increases. For a brine containing 35% $MgCl_2$ the solubility of $CaSO_4$ is 1.37 g/l. A similar trend has also been observed for $MgSO_4$. At this stage of brine concentration the sulfates are precipitated by the addition of $CaCl_2$. This treatment also results in precipitation of other solids, such as clays and silica. In exceptional cases $BaCl_2$ may be added to remove the last traces of sulfate. Following this, boron is removed by ion exchange [8] or solvent extraction [14]. In the seawater process, after $Mg(OH)_2$ has been dissolved in HCl the excess calcium is precipitated along with magnesium by the addition of sulfuric acid.

The residual sulfate is then removed by the introduction of small amounts of barium carbonate or barium chloride.

Table 2
Maximum permissible levels of impurities in electrolytic cell feed

B	0.001%
MgO	0.2%
SO_4	0.05%
Fe	0.005%
C[a]	0.2%
H_2O[a]	0.1%
Ti[b]	0.005%
Mn[b]	0.1%

[a] For anhydrous feed.
[b] For $MgCl_2$ recycled from Ti, Zr plants.

When cell feed is prepared by carbochlorination of magnesium oxide, impurities are removed by different reactions. For example, the other oxides present as impurities in MgO are also carbochlorinated by reactions such as

$$CaO_{(s)} + C_{(s)} + Cl_{2(g)} = CaCl_{2(l)} + CO_{(g)} \tag{20}$$

$$2Fe_2O_{3(s)} + 3C_{(s)} + 6Cl_{2(g)} = 4FeCl_{3(v)} + 3CO_{(g)} \tag{21}$$

$$SiO_{2(s)} + 2C_{(s)} + 2Cl_{2(g)} = SiCl_{4(v)} + 2CO_{2(g)} \tag{22}$$

$$2Al_2O_{3(s)} + 3C_{(s)} + 6Cl_{2(g)} = 4AlCl_{3.(v)} + 3CO_{2(g)} \tag{23}$$

These reactions waste chlorine and carbon. Furthermore, not all the above reactions go to completion, and the remaining oxides, particularly SiO_2, MgO, and Al_2O_3 form a slag, the removal of which complicates the operation.

Sulfates are also chlorinated according to the following reactions:

$$MgSO_{4(s)} + C_{(s)} + Cl_{2(g)} = MgCl_{2(l)} + SO_{2.(g)} + CO_{2(g)} \tag{24}$$

$$CaSO_{4(s)} + C_{(s)} + Cl_{2(g)} = CaCl_{2(l)} + SO_{2(g)} + CO_{2(g)} \tag{25}$$

Finally, up to 50% of the moisture present can evaporate upon introduction into the furnace, while the rest is chlorinated according to the reactions

$$2H_2O_{(v)} + 2Cl_{2(g)} + C_{(s)} = 4HCl_{(g)} + CO_{2(g)} \tag{26}$$

$$H_2O_{(v)} + Cl_{2(g)} + C_{(s)} = 2HCl_{(g)} + CO_{(g)} \tag{27}$$

4. Implications for producing electrolytic cell feed

It is somewhat ironic that the least dense structural metal, magnesium, which can reduce energy consumption when used as a material for vehicular construction, is one of the most energy-intensive metals to produce with presently available technologies. Thus efforts to reduce the cost of production must address the energy requirements of extraction and bring them closer to the theoretical minima. An understanding of the scientific principles of the relevant chemistry and electrochemistry serves to specify these theoretical limitations and to guide research and development in this regard.

In electrolytic processes, high-purity cell feed preparation is energy-intensive. New chemistries for energy-efficient dehydration of $MgCl_2$ may be found through better understanding the dehydration process. As for the electrolysis operation itself, improvements in energy efficiency will accrue from decreasing the cell voltage. This can be accomplished through changes in cell design and the use and development of new materials. New cell designs must reduce internal cell resistance. Improved diaphragmless cells and bipolar-array electrode configurations are two possibilities that in the past have not been fully exploited due to materials limitations. However, the advent of a new generation of high performance materials now offers a new opportunity for success. For example, some of the candidate materials for inert anodes [16] and wettable cathodes [17] that have been researched by the aluminum industry may find utility in advanced magnesium cell designs. Last, and most radically, is the prospect of totally avoiding chloride metallurgy by direct electrolysis of MgO from a molten oxide electrolyte to produce magnesium metal and oxygen gas [18].

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