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KINETICS OF THE CHLORINATION OF MAGNESIUM OXIDE

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Based on a M.S. thesis submitted to Iowa State University

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Kinetics of the chlorination of magnesium oxide

by

Ralph Niels Hesson

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NOMENCLATURE

A_g	= external surface area of grain
A_p	= external surface area of particle
b	= stoichiometric coefficient in reaction equation
C_{Ao}	= bulk molar concentration of A
C_i	= oxygen mole fraction for gas sample i
C_{is}	= surface molar concentration of species i
D_{AB}	= bulk diffusion coefficient
D_{AB_e}	= effective bulk diffusivity
D_e	= effective gas diffusion coefficient
D_K	= Knudsen diffusion coefficient
D_{K_e}	= effective Knudsen diffusivity
$D(r)$	= pore size distribution function
d_p	= diameter of solid particle
F	= inlet flow rate read directly from rotameter
F'	= inlet flow rate at 25°, 1 atm
F_g	= shape factor of grain
F''_i	= exit gas flow rate, at STP, for gas sample i
F_p	= shape factor of particle
$g_F(X)$	= conversion function
k_g	= reaction rate constant
k_s	= mass transfer coefficient
K_E	= equilibrium constant
M	= weight of one gram mole of MgO
N_A	= mole fraction of A

P	= external pressure
$P_{FP}(X)$	= conversion function
P_o	= operation pressure of rotameter
r	= pore radius
r_p	= radius of solid particle
R	= universal gas constant
R_i	= average conversion rate of the sample for the time between gas injection i and $i + 1$
t	= time
T	= temperature
t_i	= the time that gas sample i was injected
t^*	= dimensionless time
W	= initial sample weight
V_g	= volume of grain
V_p	= volume of particle
X	= fractional conversion of solid
X_{i+1}	= total sample conversion at time when gas sample $i + 1$ was injected
α	= ratio of flux of C to A
ϵ_p	= porosity of particle
θ	= contact angle
ρ_s	= molar density of solid reactant
σ	= reaction modulus
σ_s	= surface tension of liquid
τ	= tortuosity factor

Kinetics of the chlorination of magnesium oxide¹

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The chlorination reaction of MgO ($\text{MgO} + \text{Cl}_2 \longrightarrow \text{MgCl}_2 + 1/2 \text{O}_2$) was investigated by an apparatus designed to measure the product gas O_2 concentration. Reaction of a packed bed of 1.0 μ diameter particles changed from an initially reaction controlled regime to a diffusion controlled regime as the MgCl_2 product layer thickened. The "grain model" proposed by Szekely, Evans and Sohn, approximated the data quite well, except at long reaction times, when the effects of sintering of the product layer and pore closure became pronounced.

Using the "grain model", an Arrhenius-type rate expression was determined for the temperature range of 510°C to 643°C: $k(\text{cm/sec}) = 31.8 \exp(-28.0\text{kcal}/RT)$. The effective diffusion coefficient for Cl_2 in the MgCl_2 product layer was also determined.

The preparation method and thermal history of the MgO greatly varied both its surface area and reactivity. The MgO prepared by hydrolyzing MgCl_2 at 550°C was 14 times more reactive and had 23 times less surface area than MgO prepared by dehydrating $\text{Mg}(\text{OH})_2$ at 550°C. Sintering the MgO before reaction reduced its reactivity, while not changing its surface area greatly; indicating that surface diffusion and recrystallization of the MgO might have occurred.

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INTRODUCTION

Today, much of the world's energy requirement is derived from petroleum or natural gas, two fuels which are highly favored because they're easily transported and stored. For mobile applications, petroleum products are almost used exclusively because of their high energy content to weight ratio and ease of containment.

The late 1973 Arab oil embargo forced the world to realize that fossil energy sources, primarily oil, are finite in abundance. This realization has spurred investigations into alternate sources of fuels. Among the sources being examined are solar, nuclear and geothermal energy. These primary energy sources are, however, actually high temperature heat sources and for many applications it is desirable to upgrade this to a more usable secondary energy form. An ideal energy carrier would be one that would be derived from inexhaustible materials, be convenient and efficient in manufacture, be easily stored and transported, and be environmentally clean when used. Both hydrogen and electricity are such secondary energy sources.

Today the demand for H_2 is low. The U.S. consumption in the year 1973 was 3 trillion cubic feet (22), with 93% of this being "captive" hydrogen which was produced and used on-site. This compares to a yearly natural gas consumption of 23 trillion cubic feet (62). As petroleum reserves dwindle the rationale of changing to hydrogen, as an energy carrier, become apparent.

Today the major source of hydrogen is from the steam reforming of natural gas and naphtha (12). For nations like the U.S. with large coal and oil shale reserves, the gasification of coal offers a temporary source of hydrogen as petroleum products become scarce. However, less fortunately endowed nations, may be forced to consider nonfossil synthetic fuels much earlier.

Considerable work has been done in examining the prospects of a hydrogen energy economy. The results of studies on hydrogen transportation, storage and production are readily available (4, 7, 12, 18, 21, 63).

Some alternate methods of hydrogen production are: electrolysis of water, thermochemical processes, and direct thermal decomposition of water. The latter method is currently technically unfeasible. The necessary decomposition temperature of 2000°C, as well as methods to prevent recombination of the water are realistically unattainable.

The production of hydrogen by electrolysis has been commercially used for over forty years (12). The largest facility is at Rjukan, Norway, and has a capacity of 5 million cubic feet of hydrogen a day. Technology used in existing plants is obsolescent. The long-term economic feasibility of electrolysis will depend on low capital costs, high efficiency and most important the cost of electrical power. Current electrolysis efficiencies are about 22%, due mainly to the low efficiency in electricity generation. It has been speculated that with improved electricity generation methods and high pressure electrolytic cells a 50% efficiency is attainable (12,40).

A closed cycle, thermochemical hydrogen process, is designed to split water into hydrogen and oxygen using only heat energy and water, via a series of chemical reactions. All the other compounds in the process can be recycled. Theoretical efficiencies of 50% and higher are not uncommon for some of these processes. Literally hundreds of cycles have been proposed, some of the more promising ones have been tabulated by Yeh (64) and Haag (22).

The use of a water-chlorine reaction to liberate oxygen is common to many of these cycles. The reverse Deacon reaction

is one such reaction. This highly corrosive, gas phase reaction requires temperatures of 650-850°C to achieve reasonable conversion rates. The energy required to separate the gas mixture of Cl_2 , HCl and O_2 is very critical in determining the efficiency of a thermochemical process using the reverse Deacon reaction (36). For this reason another water-chlorine reaction, with easier gas separation properties is of interest.

The chlorination-hydrolysis reactions of magnesium oxide,

if operated in an alternating pattern, eliminate the costly HCl-O_2 separation as well as requiring lower temperatures. The net sum of these reactions is the reverse Deacon reaction. The kinetics of the

hydrolysis reaction were recently examined by Haag (22) and da Cunha (10). Haag reported conversions of over 95% in 30 minutes, at a temperature of 690°C.

The chlorination of MgO appears to be difficult as well as being poorly understood. Preliminary work performed at the Ames Laboratory (28) showed a rapid initial rate followed by a very slow reaction, with an overall conversion of 6.5% in 80 minutes, at 550°C. A subsequent examination by Haag (22) showed a conversion of 85% in 60 minutes, at a temperature of 570°C.

These two results are not necessarily contradictory. As with any gas-solid reaction, the reactant's surface area, pore size distribution, and preparation history have a marked effect on its reactivity. Total surface areas ranging from 120 to .05 m²/g have been reported for MgO prepared by low temperature dehydration of Mg(OH)₂ and by sintering such MgO at 1600°C respectively (19, 35).

During the chlorination of MgO, there is a 364% increase in volume because of differences in product and reactant densities. This was confirmed in a study by the Bureau of Mines (13) where MgO was chlorinated using CO as an additional reducing agent. Because of the volume change, MgCl₂ rapidly filled the pores on the surface, stopping the reaction. By placing the MgO into an inert porous bed, conversion was increased. It is apparent that a careful characterization of the sample's structure is necessary to accurately examine the reaction.

LITERATURE REVIEW

Any expression for the rate of reaction of a material, is simply a mathematical representation of a conceptual model. If this model corresponds closely to what really takes place, the expression derived from the model will closely predict and describe the actual kinetics. In order to obtain a model from which a solvable set of equations can be developed, assumptions must often be made.

A schematic representation of a solid particle undergoing a reaction with a gas is shown below.

The overall reaction process may involve the following steps:

1. Gas phase mass transfer from the gas stream to the external particle surface
2. Diffusion of the reactant gas through the pores of the particle
3. Adsorption of the gas on the surface of the particle
4. Chemical reaction on the particle surface
5. Desorption of the gaseous product from the particle surface

6. Diffusion of the gaseous product through the pores of the particle

7. Gas phase mass transfer of the gaseous product from the external particle surface to the gas stream.

If the reaction is exothermic or endothermic, the aforementioned steps will be accompanied by:

1. Heat transfer (convective and radiative) between the gas stream and the particle surface.

2. Heat conduction within the solid particle.

During the course of the reaction, various structural changes can occur. Differences in product and reactant density will result in porosity changes. Sintering of the particle can cause pore closure and reduction of surface area.

An ideal, generally applicable model would incorporate all of these effects. In most models to date, however, numerous simplifying assumptions about the reaction mechanism have been made. A relatively simple model was proposed by Levenspiel (33) for a non-porous, spherical particle undergoing an isothermal, irreversible reaction of the form:

One visualizes that reaction first occurs at the outermost surface of the particle. The reaction zone then moves into the solid leaving behind a layer of inert product (ash) as shown below.

For this "shrinking core" model, Levenspiel offered mathematical expressions for three limiting cases. If the gas phase mass transfer to the particle's surface is the rate limiting step, the time-conversion relationship is (33):

$$t = X \left(\frac{\rho_s d_p}{6bk_s C_{Ao}} \right) \quad (1)$$

t = time

X = fractional conversion of the particle

ρ_s = molar density of solid reactant

d_p = diameter of solid particle

b = stoichiometric coefficient in reaction equation

k_s = mass transfer coefficient

C_{Ao} = bulk molar concentration of A.

This is derived by relating the decrease in the particle's volume with reaction to the rate of transfer of reactant gas to the particle's surface.

If the diffusion rate through the ash layer is rate controlling, the time-conversion relationship is (33):

$$1 - 3(1 - X)^{2/3} + 2(1 - X) = \frac{6bD_e C_{Ao} t}{\rho_s r_p^2} \quad (2)$$

D_e = effective gas diffusion coefficient

r_p = radius of solid particle

This is developed assuming quasi-steady state conditions for diffusion of A through the continually thickening ash layer.

The third limiting case is that of chemical rate control; the diffusional processes are rapid compared to the surface reaction. The time-conversion relationship is (33):

$$1 - (1 - X)^{1/3} = \frac{bktC_{Ao}}{\rho_s r_p} \quad (3)$$

The rate of reaction is merely proportional to the surface area of the unreacted core.

The boundary of the unreacted material in Levenspiel's model might not be as sharp as proposed but nevertheless this model has shown good agreement with many experimental observations (6, 17, 30, 38, 57).

In recent years, models incorporating the structural characteristics of the solid have been developed; the "grain" model (Szekely and Evans (50)) and the "pore" model (Szekely and Evans (50); Chu (9)) illustrate the key developments in this area. These models, like Levenspiel's, are for isothermal, first-order reactions and make no allowance for structural changes during the reaction.

In the grain model, one visualizes a porous particle consisting of uniformly sized and spaced smaller particles, called grains. The

gas diffuses through the interstices and then reacts with the individual grains in accordance with the shrinking core model. Continually increasing concentric shells form around the grains as depicted below:

The general time-conversion expression for this model is (54):

$$\frac{bk(C_{As} - C_{Cs}/K_E)}{\rho_s(1 - \epsilon_p)} \left(\frac{A_g}{F_g V_g}\right)t = g_{F_g}(X) + \frac{k}{2D_e} \left(1 + \frac{1}{K_E}\right) \frac{V_p}{A_p} p_{F_p}(X) \quad (4)$$

where $g_{F_g}(X) = 1 - (1 - X)^{1/F_g}$ (5)

$p_{F_p}(X) = X^2$ for flat particles ($F_p = 1$) (6)

$p_{F_p}(X) = X + (1 - X)\ln(1 - X)$ for cylindrical particles ($F_p = 2$) (7)

$p_{F_p}(X) = 1 - 3(1 - X)^{2/3} + 2(1 - X)$ for spherical particles
($F_p = 3$) (8)

C_{is} = surface molar concentration of species i

K_E = equilibrium constant

ϵ_p = porosity of particle

A_g, A_p = surface area of an individual grain and particle respectively

V_g, V_p = volume of grain and particle respectively

F_g, F_p = shape factor of grain and particle respectively.

This expression is very similar to those of Levenspiel, with the improvement of accounting for reversible reactions, porosity and the effect of pore diffusion. For the limiting cases of chemical reaction rate control and ash layer diffusion control, the expression reduces to the same equations presented by Levenspiel.

Szekely defined a parameter called the "reaction modulus" for his model (52),

$$\sigma = \frac{V_p}{A_p} \sqrt{\frac{(1 - \epsilon_p) k_F}{2D_e} \left(\frac{A_g}{F_g V_g} \right) \left(1 + \frac{1}{K_E} \right)} \quad (9)$$

which is simply arrived at by rearranging his general reaction expression into the form:

$$t^* = g_F (X) + \sigma^2 p_F (X) \quad (10)$$

t^* = dimensionless time; time divided by the time to reach total conversion.

For values of σ less than 0.3 the reaction being studied can be treated as chemically controlled (47). Similarly, for a σ greater than 3.0 the reaction can be treated as being under diffusional control. For exact solutions of the general expression, numerical methods must be employed.

Since the first presentation of the grain model in 1970 (50), subsequent studies (16, 39, 46, 48, 49, 51, 53, 54) have modified the

model to take into account more structural variables. The effects of sintering, nonisothermal behavior, reaction order, pore and particle size distributions and continually changing grain sizes have been studied and incorporated into the mathematic expressions for the model... Kim and Smith (32) and Ramachandran and Smith (42) have developed complex models which include the effects of sintering.. For Ramachandran's model, however, except for the hydrofluorination of UO_2 no system has been studied adequately to provide the kinetic, sintering data required. As can be expected, most of these more complex models result in expressions which must be numerically solved.

For gas-solid reactions in which the molar volume of the product is different than that of the reactant, the grain model often proves inadequate. The porosity of the particle can increase with reaction, giving a continual rise in the surface area, or as in the sulfonation of CaO ,

result in pore closure (26, 39). Experimental data for this reaction shows that the CaSO_4 is virtually impervious to the SO_2 . Because of the 2.7 fold increase in molar volume the pores plug up and reaction ceases well short of complete conversion. Hartman and Coughlin (25) were able to predict the conversions of CaO samples by simple porosity change calculations based on reactant and product molar volumes and use of the grain model. Their porosity-conversion calculations show that it's realistic to assume that all reaction occurs internally.

Ramachandran and Smith (41) have developed a "single pore" model which takes the plugging effect into account. One visualizes a particle which consists of a number of cylindrical pores of finite length. The reactant gas diffuses into the pore and the reaction front moves radially and axially as shown below.

As the reaction proceeds, the pore diameter decreases, and diffusional resistances (ash layer and pore) increase. This model has shown good agreement with CaO-SO_2 reaction data. A similar model has also been developed by Chrostowski and Georgakis (8).

For most of the models, average pore and particle size, as well as effective gas diffusivities must be known. Standard methods for particle size analysis and porous media characterization have been recently reviewed by Davies (11) and Dullen and Batra (14) respectively. Szekely, Evans and Sohn (54) have also given a good survey of solids characterization methods.

The gas diffusivities can be readily predicted using the Chapman-Enskog equation for bulk diffusivity and various kinetic theory relations are available to find the Knudsen diffusivity (2, 45, 54).

A correction for the porosity and tortuosity of the particle must be made,

$$D_{AB_e} = \frac{D_{AB} \epsilon p}{\tau} \quad (11)$$

$$D_{K_e} = \frac{D_K \epsilon p}{\tau} \quad (12)$$

D_{AB} = bulk diffusion coefficient

D_K = Knudsen diffusion coefficient

D_{AB_e} , D_{K_e} = effective bulk and Knudsen diffusivity respectively

τ = tortuosity factor; experimental parameter accounting for the tortuous diffusion path.

then the effective diffusivity for the particle can be calculated (56).

$$D_e = \frac{1}{(1 - (1 - \alpha)N_A)/D_{AB_e} + (1/D_{K_e})} \quad (13)$$

α = ratio of flux of C to A

N_A = mole fraction of A.

A thorough explanation of the calculation procedure can be found in Satterfield (45).

The only comparison of the kinetics of the chlorination of MgO to a model has been by Ishii et al. (30). His study was on the chlorination of mixtures of MgO and graphite. This mixture chlorinated quite rapidly. With molar ratios of carbon to magnesium of 0.5 and 1.0, conversions of 19% and 33% were observed for reaction at 500°C, for one hour. The added graphite acts as a reducing agent and consumes all of the oxygen produced. It is also believed that some catalytic effect or formation of Cl-C radicals are involved (31, 38, 58).

Ishii was able to fit his data to the Jander equation, an approximate solution of the ash layer, diffusion-controlled shrinking core model. He also reported that there is no chlorination of pure MgO at a temperature of 650°C.

EXPERIMENTAL EQUIPMENT

The conversion of the solid reactant with time can be measured using several different methods. The most widely used is thermogravimetric analysis. The solid sample is suspended in the reaction furnace from a recording balance. As the reaction proceeds, the weight change of the sample is continuously monitored.

Another method, is by batch analysis of the solids (26, 63). Reaction is stopped at incremental times and the conversion of the solids is determined by direct analytic methods. A large number of runs have to be carried out to get the equivalent data obtained from one run using a continuous analysis method.

A continuous monitoring method, not often used, is based on off-gas measurements. The flow rates and concentrations of the reactant gas stream are measured and the solid's conversion can be back calculated from these data. Since a gas chromatograph capable of separating chlorine and oxygen was available, this method was chosen.

The reaction vessel used for the chlorination runs is shown in Figure 1. It is very similar in design to the one used by Haag (22) in his hydrolysis study of MgCl_2 . With the exception of the graded seal and ball joint the reactor is made of quartz. A section 24 mm in diameter is filled with quartz chips to allow adequate gas preheating. The reaction zone of the vessel is 8 mm in diameter and has a dimple at the base of the reaction section. The sample is supported by Tioouoquartz 2500 QAST, a high temperature quartz cloth manufactured by Pall, which is placed on 6 mm diameter quartz tubing supported by

Figure 1. Chlorination reaction vessel

the dimple. This arrangement allows the sample's height in the reactor to be varied. The feature will become important when temperature profiles in the furnace are discussed.

The furnace used for heating the reactor to operating temperatures was a Lindberg Model 54341 Tube Furnace placed in a vertical position. A Lindberg Solid State Digital Controller Type 2200 capable of an accuracy of $\pm 1^\circ\text{C}$ was coupled to the furnace. Although the furnace was capable of excellent temperature control and reproducibility, temperature profiles in the reaction zone were desired. These are discussed in the Experimental Work section.

The gas analysis was done with a Carle Instruments Model 111 Analytic Gas Chromatograph, equipped with a .25 ml tantalum sampling valve. The chromatograph's two tantalum columns were specified to separate $\text{Cl}_2\text{-O}_2\text{-CO}_2$ mixtures and the gas streams were analyzed with thermal conductivity detectors (thermistors). Matheson high-purity helium was used for the purge gas. The analyzed gas stream was bubbled through a NaOH solution for purification, then vented.

Linde high-purity chlorine gas was used and dried by bubbling through concentrated H_2SO_4 . Flow rate was monitored by a Brooks chlorine rotameter. A schematic representation of the equipment set-up is shown in Figure 2. When reduced partial pressures of chlorine were being used, an additional Century rotameter was added to the system. A photograph of the chlorination equipment is shown in Figure 3.

A homogeneous MgO supply of known preparation history was desired. Since the chlorination reaction is theorized to be run back-to-back with the hydrolysis of MgCl_2 ; the MgO supply was produced by batch

Figure 2. Schematic diagram of chlorination equipment

Figure 3. Experimental equipment for a chlorination run

hydrolysis of reagent grade MgCl_2 . The reactor used for this was very similar to the chlorination reactor, with the major exception that it was all 24 mm in diameter (Figure 4). A porous quartz disc was used to support the MgCl_2 bed. Steam for the reaction was generated in a stainless steel U-tube contained in an electrically heated graphite block. Water was injected into one end of the tube by a Sage Instrument Model 355 syringe pump. A schematic representation of this system is shown in Figure 5.

Pore size distributions and sample densities were determined with a Micromeritics Model 910 Series Mercury Penetration Porosimeter. A discussion of its operation will be given later.

Determination of Solid's Conversion by Titration

Unweighed samples (approximately .2 g) were added to 25 ml of water. Enough concentrated nitric acid (HNO_3) was added in order to dissolve the sample, approximately 1 ml was required for a pure .2 g MgO sample. This solution was pipetted equally into two clean beakers.

Analysis for Cl^- was made by using Mohr's titration (5, 59) with .0300 M silver nitrate (AgNO_3) and using sodium chromate (NaCrO_4) as an indicator. The pH of the aliquot was adjusted to 8 by adding calcium carbonate (CaCO_3) and the yellow solution was titrated until the formation of red silver chromate (Ag_2CrO_4) was noted.

Mg^{+2} was determined by complexometric titration of the solution using EDTA with Calmagite as an indicator (5). The solution was buffered to a pH of 10 and the endpoint of the titration was noted by a

Figure 4. Hydrolysis reaction vessel

Figure 5. Schematic diagram of hydrolysis equipment

change from red to blue. The complex is formed in a one to one EDTA to Mg^{+2} ratio. The buffer was prepared by dissolving 68 g of ammonium chloride (NH_4Cl) in 570 ml of concentrated ammonia hydroxide (NH_4OH) and by diluting to one liter.

With the Mg^{+2} to Cl^- ratio determined, the concentration of MgO and MgCl_2 could be calculated. If the system was not anhydrous and was not operated at temperatures above which magnesium oxychloride (MgOHC1) is unstable, a more extensive titration procedure would be needed (22).

Determination of Gas Concentrations, Flow Rates and the Time-Conversion Curves

The chromatograph was operated at a temperature of 45°C and a purge gas flow rate of 30 ml/min. These operating conditions were recommended by Carle Instruments. Gas calibrations were based on injections of pure gases and the assumption of linear concentration dependence to zero. For thermal conductivity detectors this is an often used assumption. As will be shown later, this calibration also gave good agreement between results calculated using chromatograph data and the titration data. Weekly fluctuations of about 4% in the oxygen calibration and up to 50% in the chlorine calibration were initially observed. With frequent correction of the chlorine column purge gas rate this high variation was eliminated. Weekly calibrations were still taken to assure accuracy.

The retention time of the chlorine is about 4 minutes so samples could be injected about every 5 minutes. After it was determined that all the helium initially used to purge the reactor was expelled, the oxygen concentration was calculated using the oxygen peak only. This point was where the oxygen and chlorine concentrations, calculated from their respective calibrations, added up to 100%. The pure chlorine feed gas had an oxygen concentration of approximately .2% which had to be subtracted off from each determination.

In Appendix A, a sample calculation of how the time-conversion results were determined is given. Briefly, the procedure is as follows:

1. Correct the inlet flow rate for the difference between rotameter operation and calibration pressure.
2. Calculate the exit gas flow rates at STP from the oxygen concentrations and the inlet flow rate.
3. Calculate the conversion rate for each sample using the oxygen concentration, sample weight, exit gas flow rate and the ideal gas law.
4. Integrate the conversion rate-time data using the trapezoidal rule.

Determination of Pore Size

Distribution and Particle Density

Mercury Penetration Porosimetry was used to determine the porosity, pore-size distribution and density of the samples. Due to its simplicity and versatility, this method has been employed in the determination of

the pore-size distribution curves of a wide variety of porous materials (3).

The surface tension of mercury (474 dynes/cm) opposes its entrance into small openings; an opposition that externally applied pressure can overcome. Any time a liquid exhibits an angle of contact greater than 90° , it will resist wetting the solid and entering any pores. Reported contact angles between mercury and a large variety of materials have a most frequent value of 130° . In the absence of specific data, this value is usually employed (3, 29).

For a pore of circular cross-section, a force balance between the external pressure squeezing the liquid into the pores and the surface forces tending to squeeze the liquid out gives the following expression (20, 29).

$$P \cdot r = - 2\sigma_s \cos \theta \quad (14)$$

P = external pressure

r = pore radius

θ = contact angle

σ_s = surface tension of liquid.

Thus for a porous solid surrounded by liquid, as the pressure increases, the quantity of liquid forced into the pores increases in proportion to the differential pore volume. The instrument used allowed the intrusion of mercury into a sample and the incremental measurement of pressure and cumulative intruded mercury.

The pore-size distribution function ($D(r)$), is defined as:

$$D(r) = \frac{dV}{dr} \quad (15)$$

dV = volume of pores having radii between r and $r + dr$.

$D(r)$ is proportional to the number of pores of radii between r and $r + dr$. This can be readily calculated from the instruments data (20), and when plotted versus pore radius gives the pore-size distribution, and thus the average pore size. The apparent sample density can be calculated from the sample weight and the volume of the mercury displaced while at a very low pressure.

EXPERIMENTAL WORK AND RESULTS

Experimental work consisted of making the experimental equipment operational and taking kinetic data on the MgO-MgCl_2 reaction.

Temperature Profiles

In order to properly support a packed bed sample it was necessary to have both the reactor and furnace in a vertical position. With the furnace vertical, convection currents caused by warmer air rising out of the furnace resulted. A large temperature variation from the bottom to top of the furnace was measured. Using tightly fitting firebrick plugs and pyrex wool, the ends of the furnace were sealed around the reactor in order to minimize this convection current effect. By extending a chromel-alumel thermocouple to various depths in the reactor and measuring the potential, temperature profiles were obtained. A temperature variance of about 12°C was measured over an 8-inch reaction zone. The setpoint temperature of the controller did not match the average temperature in the reaction zone except at high temperatures. By knowledge of the temperature profiles and the setpoints over a number of temperatures, interpolation to other temperatures and setpoints was possible.

A temperature variation of less than 1.0°C resulted in the zone between four and five inches above the dimple. The quartz tubing supporting the sample was adjusted in length to place the sample in this zone. Deviations in the profiles with changes in gas flow rate were found to be negligible. Flow rates of 11 and 22 cc/min of CO_2 produced identical profiles while at 40 cc/min a 1.5°C drop was measured.

Preparation of MgO

The MgO was produced by the batch hydrolysis of - 16 to + 200 mesh MgCl_2 , using the equipment shown in Figure 5. The reactor was charged with 50 g of MgCl_2 and reacted at 550-562°C for five hours. A water flow rate of 10 cc/hr to the steam generator was used. At the completion of a run, the reactor was purged with dry argon until cool. The MgO was immediately bottled and placed in an evacuated desiccator.

Approximately 300 g of "stock" MgO were prepared using the procedure. Analysis showed that it was 99.0% MgO and 1.0% MgCl_2 . Attempts to sieve the powder to obtain a particle size distribution proved futile. The dry MgO powder was both too cohesive and too fine to classify mechanically. The particle size distribution was obtained by a Coulter Counter analysis of an aqueous suspension of the sample. MgO is insoluble in water and the loss of the 1.0% MgCl_2 , which does dissolve, was considered inconsequential. Figure 6 shows the result of this analysis for both the stock MgO powder and powder obtained by breaking apart pellets made from the stock powder. A discussion of the results for the pellets will be given later.

Assuming spherical particles, the weight, area, and population mean particle diameters for the stock MgO were 3.59, 2.10 and 0.94 microns respectively. These results compare well to the 0.5 to 3.7 particle diameters which were optically measured from scanning electron microscope (SEM) photographs of the powder.

Figure 6. Particle size distribution for the MgO samples

The surface area of the stock MgO powder was analyzed by Micromeritics Instrument Corporation. Using a modified BET adsorption method, they reported an area of $2.23 \text{ m}^2/\text{g}$.

Chlorination of MgO Powder

The chlorination reaction was first examined by reacting a packed bed of MgO powder at various temperatures. Using a high chlorine flow rate, bulk mass transfer effects were to be eliminated. The controlling mechanism of the reaction and possibly the reaction rate constants were to be determined from these observations.

A chlorine flow rate of approximately 12 cc/min was used for these runs. It was necessary to put quartz cloth and a piece of quartz tubing on top of the sample bed to prevent fluidization and removal of sample from the reaction zone. The procedure used for all the chlorination runs was the same. The chlorine drying flask was purged for 5 minutes with chlorine to remove all the oxygen. Dry helium was then purged through the rotameter and tubing preceding the reactor. The MgO sample (usually 0.5000 g) was weighed and immediately placed in the reactor. With the quartz tubing on top, the bed thickness was approximately 0.7 in. The fully assembled system was purged with helium until the oxygen concentration, measured by the chromatograph, fell to 0.2%. The furnace was switched on and after the temperature had been steady for 20 minutes the helium was shut off. Chlorine flow and an electric timer were then started. Gas concentrations were measured about every 6 minutes and after the last measurement was taken the

furnace was opened and the system was purged with helium again. The reacted solid sample was then analyzed to determine the final conversion of the MgO .

Although numerous runs were made, difficulty in getting consistent agreement between the chromatograph's and titration's results was experienced. Factors which caused this were:

- 1) Variations in the gas flow rate because of fouling of the rotameter.
- 2) Malfunction of the chromatograph's sampling valve.
- 3) Inadequate purging of the system prior to a run.
- 4) Small gas leaks in the system.

Runs with a difference in final conversion of 10% or greater between the titration's and chromatograph's results, were discarded. The runs where the conversions were within 10% of each other had good reproducibility of the time-conversion curves (Figure 7). A comparison of some of the conversions calculated from the chromatograph's and titration's data is shown in Appendix B. The time scale for all of the conversion curves is adjusted so that time zero corresponds to when the chlorine first reaches the chromatograph. The percent conversion corresponds to the conversion that took place during the reaction and does not include the 1% MgCl_2 already present in the stock MgO . Conversion curves derived by averaging the results of several runs at each temperature are shown in Figure 8.

The reacted powder was removed from the reactor as a soft but cohesive cylindrical solid. It easily crumbled apart and as expected

Figure 7. Reproducibility for the chlorination of MgO powder at 563°C

Figure 8. Average results for the chlorination of MgO powder at a 12 cc/min Cl_2 flow rate

the higher conversion runs produced harder cylinders. This effect is accounted for by the increase in volume of the particles during reaction and the sintering of the low melting (712°C) MgCl_2 . Powders were examined with an SEM before and after reaction and the aforementioned effect is clearly noticed (Figure 9 and Figure 10). However, the porosity of the bed remained quite high. For a run at 643°C , for 100 minutes, an increase of the pressure drop through the bed from 0.36 psi to 1.04 psi was measured. Porosity studies of reacted and unreacted powder showed that the particles were nonporous. An SEM photograph of the unreacted powder (Figure 24) supports this, as well as shows that the particles are approximately spherical.

The off-gas oxygen concentrations, except for the first five minutes of the 690°C runs, were well-below equilibrium values. For the runs at 643°C an initial oxygen concentration of 6% (65% of equilibrium) decreased to less than 1% in an hour. The runs at 510°C never had an O_2 concentration over 1.5% (6% of equilibrium). The fact that the 690°C runs had oxygen concentrations approaching equilibrium values, explains the coincidence of the initial portion of their conversion curve with the 643°C curve. Carefully analyzing the solids for a run at 643°C , conversions of 24.0% at the top of the bed and 19.9% at the bottom of the bed were determined. This difference is not as small as hoped and would suggest the use of a thinner bed. With smaller sample sizes, however, the oxygen concentration in the off-gas became too small to be reliably measured. For this reason the 0.5 g sample size was still used. The conversion of the bed was considered uniform to simplify calculations.

Figure 9. Unreacted stock MgO powder (3300x)

Figure 10. MgO powder reacted at 643°C for 100 min at a 12 cc/min flow rate (3300x)

Because of the high porosity of the bed and the fact that there is forced flow, some assumptions can be made. The bed can be treated as if it were a group of individual particles undergoing a shrinking core reaction. Although the reaction is exothermic (7.3 kcal/gmole at 643°C) the bed was assumed to be isothermal because of the good gas to solid contact. The reaction is very slow and the possibility of mass transfer control is readily eliminated. Based on correlations for flow through a packed bed (54), a mass transfer coefficient of $0.0013 \text{ g moles/cm}^2 \text{ sec}$ is calculated. The time predicted to reach 100% conversion is 3.0 minutes (Equation 1), a time obviously smaller than the observed results.

Assuming the reaction takes place in the chemically controlled regime, a plot of $1 - (1 - x)^{1/3}$ versus time was made (Figure 11). The linearity of the low temperature runs and initial linearity of the higher temperature runs suggests chemical control in these areas. The curvature of the high temperature runs could be attributed to several things: increase in the ash layer diffusional resistance, sintering of this ash layer and gas channeling caused by pore closure.

The slopes for the initial 20 minutes of reaction for the curves in Figure 11 were measured and the respective reaction rate constants were calculated (Equation 3). These values conform to the Arrhenius rate expression quite well (Figure 12). If the reaction rates had been calculated in a mixed reaction control regime (diffusional and chemical) the dependence of $\ln k$ versus $1/T$ would not have been linear. The linearity in Figure 12 reinforces the hypothesis that the reaction is initially chemically controlled. The disagreement of the 690°C

Figure 11. Reaction controlled model for the chlorination of MgO powder at 12 cc/min Cl_2 flow rate

Figure 12. Arrhenius plot for chlorination of MgO powder at a 12 cc/min Cl_2 flow rate

data could be caused by the approach to equilibrium conditions, as previously mentioned.

For the limiting case of ash layer diffusional control, a plot of P_{F_g} versus T should be linear (Equations 2 and 4). Applying this fact (Figure 13), one sees that except at high conversions and the beginning of the reaction, the curves are linear. The reaction apparently undergoes a transition from the chemical to diffusional controlled regimes as conversion increases. The initial flatness of the curves is characteristic of a reaction in the chemically controlled regime. For the 690°C and 643°C data the deviations at high conversions are probably due to the sintering of the $MgCl_2$ layer. The reactions at 510°C and 537°C are believed to be chemically controlled throughout the entire reaction period. The linearity of the lowest temperature curves on both Figures 11 and 13 is not contradictory. At very low conversions chemically controlled reactions are linear on a plot of P_{F_g} versus T .

From the slopes of the linear portion of each curve in Figure 13, the effective ash layer diffusivity at each temperature could be calculated (Equations 2 and 4). These values (Figure 14) show a linear dependence upon temperature. Since Knudsen diffusivity is proportional to $T^{1/2}$ and molecular diffusivity to $T^{3/2}$ this suggests a mixed diffusional regime.

The models used to describe the data for the previous runs all assume the reaction is first order with respect to the reactant gas. For the limiting cases of chemical reaction and diffusion control,

Figure 13. Diffusion controlled model for the chlorination of MgO powder at a 12 cc/min Cl₂ flow rate

Figure 14. Effective diffusion coefficients through the MgCl_2 layer

especially at high conversions, the effect of reaction order is pronounced. The reaction rate dependence on the chlorine concentration, and hence reaction order, can be determined by doing runs at different chlorine partial pressures.

Runs were made at 643°C at four different chlorine pressures. Chlorine fed to the reactor was diluted with helium to achieve the reduced partial pressure. Two runs were made at each partial pressure to test the reproducibility of the data. Figure 15 gives a comparison of two such runs. The discrepancy between these two runs for the first 20 minutes of reaction was typical for all the runs. This was attributed to difficulties in starting up the chlorine and helium flows. The conversion curves obtained by averaging the runs at each partial pressure are given in Figure 16. For a first-order reaction, the initial slopes of the curves should be proportional to the Cl_2 partial pressure. With the exception of the curve at a partial pressure of 0.34 atm the initial slopes are nearly equal. Because of the low precision of the experimental technique in the initial reaction period the calculation of reaction rates from the slopes of the curves was not attempted. There is, however, a noticeable induction period for the lower pressure runs. This might suggest that the adsorption of Cl_2 on the particle's surface is enhanced once a MgCl_2 layer has formed. A similar observation has been made in the reduction reaction of NiO with H_2 (55).

Figure 15. Reproducibility for the chlorination of MgO powder at 643°C and reduced Cl₂ partial pressure

Figure 16. Average results for the chlorination of MgO powder at 643°C and reduced Cl₂ partial pressure

Chlorination of MgO Pellets

To obtain data for which a model incorporating pore closure effects could be applied a porous particle must be studied. Cylindrical pellets were made by compressing the stock MgO powder in a die at a pressure of 24,500 psi. The pellets were 3.1 mm long and 6.4 mm in diameter, with an average weight of 0.2 g apiece. The pellets were limited to this small size for two reasons. First, they had to be small enough to allow gas flow around them in the 8 mm reactor. Secondly, because of the nonisostatic compression in a cylindrical die they had to be less than 1 diameter in height to still have uniform porosity. From the average weight and size measurements of the pellets, an average porosity of 0.44 was determined. The pellets were hard enough to be handled without crumbling, but could be broken apart by vigorous shaking in a bottle. Coulter Counter analysis of a crumbled pellet showed that the grains of the pellets decreased slightly in size from the uncompressed stock MgO powder. The size distribution is shown in Figure 6. The size reduction is due to the fracturing of the grains as they are compressed. The weight, area and population mean particle diameters were 2.44, 1.40 and 0.80 microns respectively. A total surface area of $1.17 \text{ m}^2/\text{g}$ was measured by Micromeritics Instrument Corporation. This surface area is half of that of the uncompressed powder and indicates that many sealed pores exist in the pellet.

A single pellet was used in each run and because of the small sample size all runs were done at a temperature of 643°C in order to get higher oxygen off-gas concentrations. Reactions at various flow

rates were made in an attempt to determine if bulk mass transfer to the pellet surface was controlling the reaction. The pellets appeared to be uniformly reacted and were very hard. They had to be crushed in a mortar for titration work. The reproducibility of the runs at a flow rate of 11.5 cc/min and the average curves for all the runs are shown in Figures 17 and 18 respectively.

The conversion of the pellets decreased as the gas flow rate was increased. This was a completely unexpected result. It is opposite of what would occur for a mass transfer controlled reaction as well as being different from the "no change" result, characteristic of a nonmass transfer controlled reaction.

This decrease in conversion cannot be attributed to temperature differences between the pellets as one might first expect. Because the reaction is exothermic, the pellets could initially heat up above the reaction zone temperature and in the higher gas flow rate runs cool down faster. At long reaction times, however, the rates have slowed sufficiently that the temperatures of the pellets should be close to the reaction zone temperature; all reaction rates should be equal. Even after 100 minutes, though, the reaction rate of the low gas flow runs are 4 times that of the rate for the 46 cc/min runs. Because of the rapid flattening of the conversion curve of the runs at 46 cc/min, it appears as if plugging of the pores might have occurred. Insight into the pore structure and change of pore structure with reaction might help to explain why the conversions dropped with increasing flow rates. Possibly the pores near the external surface plug up more rapidly at the increased flow rates.

Figure 17. Reproducibility for the chlorination of MgO pellets at 643°C

Figure 18. Average results for the chlorination of MgO pellets at 643°C and different chlorine flow rates

Pore size distributions for the unreacted and reacted pellets were determined with a mercury penetration porosimeter. Four pellets had to be analyzed at one time in order to get a sufficiently large sample size. The distribution curves (Figure 19) show that the pore radius at the volume modal, for the unreacted and reacted pellets, is about equal; 0.17 and 0.16 microns respectively. The porosity, however, changed from 0.42 to 0.30. The porosity for the unreacted pellet, calculated with the porosimeter, differed by only 5% from the porosity previously calculated by weight and volume measurements. Since the pore radii of the reacted and unreacted pores are nearly equal, the idea of selective pore closure near the surface no longer seems credible. SEM photographs of the surface of an unreacted and reacted pellet, Figure 20 and Figure 21, also show this. Assuming that all reaction takes place internally, the porosity of the reacted pellet can be predicted by knowing the porosity of the unreacted pellet and the final conversion of the pellet. This calculation predicts a porosity of 0.27 for the reacted pellet, quite close to the actual value of 0.30. This good agreement parallels Hartman's and Coughlin's (25, 26) observations on CaO and suggests that a pore plugging model might be applicable to the system.

After plotting P_F versus temperature for the reaction of the pellets (Figure 22) one sees that the reaction is not purely ash layer diffusion controlled because of the nonlinearity of the curve. A calculation of the reaction modulus (σ) using an effective pore diffusivity of $0.033 \text{ cm}^2/\text{sec}$, gives a value of 0.19. This indicates chemical reaction control at the onset of the reaction. A value of 6040

Figure 19. Pore size distributions for the unreacted and reacted pellets

Figure 20. Surface of unreacted pellet
(3000x)

Figure 21. Surface of pellet reacted at
643°C for 100 min at a
12 cc/min Cl_2 flow rate
(3000x)

Figure 22. Diffusion controlled model for the chlorination of MgO pellets at 643°C

for σ is calculated using the MgCl_2 layer diffusivity; showing that diffusion through the MgCl_2 layer assumes control almost immediately.

As evidenced by the rapid decrease in reaction rate for the pellets, a layer of MgCl_2 must rapidly cover the entire surface of the pores. The diffusion coefficient of the MgCl_2 layer ($4.6 \cdot 10^{-11} \text{ cm}^2/\text{sec}$ at 643°C) is as small as some diffusivities in the solid state (15). This is not surprising, considering the reaction temperature is only 69°C below the MgCl_2 fusion temperature and rapid sintering is probably occurring. In addition to the sintering effect, the closing of pores as reaction continues may as well cause the deviation from the diffusion controlled model. A large number of "bottle necked" pores, pores with small entrance diameters but large actual diameters, would make the effect of pore closure very large. Because of the difficulty in studying small sample sizes with the current equipment, experimentation with pellets was discontinued.

Effect of Additives on Chlorination Rate

Increased conversions have been reported for mixtures of MgO with porous solids and mixtures with carbon (27, 30). Runs were made for both of these cases in order to determine the effect of these additives. Firebrick, crushed and sieved at - 180 to + 200 mesh was used as an inert filler. This firebrick was 50% Al_2O_3 and 50% Si_2O_3 , both of which do not chlorinate below 1200°C (62). Equal weights, 0.5000 g, of the inert and the stock MgO powder were mixed and charged into the small reactor. At 643°C and a flow rate of 12 cc/min

of chlorine the average conversion for three runs was 24% in 106 minutes. This compares to about 20% conversion for the plain packed bed. The fact that the inerts caused only a slight increase in conversion is not surprising. The only effect the inerts would have would be to decrease the pore diffusional resistance in the bed. Since the bed experiences forced gas flow, however, this resistance should be negligible, even without the increased porosity. It was this fact that allowed the bed to be considered a collection of reacting solid grains as opposed to a reacting porous solid.

Powdered graphite was mixed with stock MgO and reacted at 643°C. The conversion curves for two runs made at different C-Mg mole ratios are shown in Figure 23. The reacted solids were very hard and had a glazed appearance. Both runs had an initial rapid reaction rate followed by a sudden decrease in rate. About 30% of the carbon remained unreacted. This indicates that not the depletion of carbon but some other reason was responsible for the abrupt slow-down of the reaction. This observation was also made by Ishii et al. (30). The reaction between MgO, Cl₂ and carbon (30),

is very exothermic (44.3 kcal/g mole at 643°C). Ishii measured temperature rises for C-MgO samples of over 100°C in the first 20 minutes of reaction. Rapid sintering and maybe melting of the MgCl₂ layers, which resulted in increased diffusional resistance, probably stopped the reaction.

Figure 23. Chlorination of MgO powder with C at 643°C.

Effect of MgO Preparation History on Chlorination Rate

The stock MgO was produced by hydrolyzing MgCl_2 in order to have a sample simulated as coming from a MgO- MgCl_2 cycle. The surface area of the MgO produced by the method was quite low, $2.23 \text{ m}^2/\text{g}$. Dehydrating $\text{Mg}(\text{OH})_2$ at 550°C until a constant weight was measured (10 hours), a MgO sample with a surface area of $53.0 \text{ m}^2/\text{g}$ was produced. SEM photographs of stock MgO powder and the powder produced by dehydration of $\text{Mg}(\text{OH})_2$ are shown in Figures 24 and 25 respectively.

The new MgO powder is comprised of almost perfectly spherical particles. By optically measuring and counting particles from SEM photographs an approximate particle size distribution was determined. The weight, area and population mean particle diameters were 33, 20 and 2.2 microns respectively. The porosity of this powder was not determined but intuitively it must be quite high.

The conversion curve for a run on the new MgO (Figure 26) shows almost a linear dependence with time except for a slight induction period. Since the surface area is very high a large conversion is realized (42%) before the MgCl_2 layer thickens enough for diffusional effects to be seen (Figure 27). The reaction rate constant for this run was $4.3 \cdot 10^{-7} \text{ cm/sec}$, more than 14 times smaller than that of the stock MgO. This result shows that the reactivity of MgO is strongly dependent on the preparation method.

In an attempt to produce a very unreactive MgO powder, some stock powder was held at 960°C in a muffle furnace for four hours. This powder was then chlorinated at a temperature of 643°C with a flow

Figure 24. Unreacted stock MgO powder (11,000x)

Figure 25. Unreacted MgO powder produced from Mg(OH)_2 (450x)

Figure 26. Chlorination of MgO powder produced from $\text{Mg}(\text{OH})_2$

Figure 27. Reaction controlled model for the chlorination of MgO powder produced from $\text{Mg}(\text{OH})_2$

rate of 12 cc/min of Cl_2 . The conversion was only 2.1% after 100 minutes of reaction. The surface area of the powder used in this run was $2.3 \text{ m}^2/\text{g}$, identical to that of the stock MgO powder. The conversion, however, was one order of magnitude less. The only explanation for this could be that recrystallization and surface diffusion of the MgO had occurred. The elimination of point defects in a solid will reduce the solid's reactivity (24). At temperatures as low as 26% of the fusion temperature these clarifying effects are seen in metal oxides (15). A powder sample was held at 643°C for 20 hours in helium and then reacted. Its conversion was only 9.5% after 100 minutes of reaction, less than half of a sample which is chlorinated without heat treatment. Even at the relatively low temperatures for the runs, this clarifying of defects was occurring.

CONCLUSIONS

The exploratory work presented in this thesis enables the following conclusions to be reached.

1. The reaction rate constant for the chlorination of MgO can be expressed by the Arrhenius expression; $k(\text{cm/sec}) = 31.8 \cdot \exp(-28,000 \text{ cal/RT})$, assuming a first order reaction model.

2. Thermal treatment of MgO decreases its reactivity while not necessarily changing its surface area. This fact may suggest surface diffusion and recrystallization in the MgO occur.

3. Chlorination of MgO powder is initially chemical rate controlled. This rapidly changes to diffusional control as the MgCl_2 layer thickens. At temperatures above 617°C , sintering of the MgCl_2 layer noticeably decreases the reaction rate.

4. Assuming a first-order reaction model, the effective diffusion coefficient for Cl_2 flow through the MgCl_2 layer, between 836°K and 963°K , can be expressed as: $D_e(\text{cm}^2/\text{sec}) = 4.7 \cdot 10^{-13} T - 3.85 \cdot 10^{-10}$.

5. Chlorination of the MgO pellets is controlled by a combination of pore and ash-layer diffusion. The conversion of the pellets can be accurately correlated to the porosity changes experienced in the reaction. This suggests a pore-plugging model might accurately describe the reaction.

6. MgO prepared by dehydrating $\text{Mg}(\text{OH})_2$ is high in surface area and porosity, and has a wide particle size distribution. MgO prepared by hydrolyzing MgCl_2 is low in surface area, nonporous, and has a very narrow particle size distribution. Thus, by changing the MgO

preparation method and conditions the MgO chlorination rate can be greatly varied.

It is stressed that unless the above statements are associated with the experimental conditions (particle size, temperature, gas velocity, etc.), the results of this study may be misleading. Gas-solid reactions are quite complex and are affected by many phenomena.

RECOMMENDATIONS

From the results of this exploratory work the following recommendations are offered for future research:

1. Investigate more intensively the chlorination of porous MgO samples. One such study should focus on determining the reaction order, pore diffusion coefficients, and the effects of porosity. The use of a recording balance is recommended in order to achieve the necessary measurement precision.
2. A study of the effect of sintering on the pore diffusion in MgCl_2 pellets should be made. This study will help to determine the optimum MgO-Cl_2 reaction temperature.
3. Investigate the possibility of using a fluidized bed instead of a packed bed. The addition of inerts into the fluidized bed should also be examined.
4. A preliminary economic comparison of the reverse Deacon reaction and the MgO-MgCl_2 cycle should be made. The minimum operating costs would be realized if the MgO-Cl_2 reaction could be operated in a chemically controlled regime.

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APPENDIX A.

CALCULATION METHOD FOR OBTAINING THE TIME-CONVERSION

CURVES FROM THE EXPERIMENTAL DATA

$$1) \quad F' = F\sqrt{(14.7 + P)/P} \quad (16)$$

F' = inlet flow rate at 70°, 1 atm

F = inlet flow rate read directly from rotameter

P_o = operation pressure of rotameter.

This correction equation was supplied with the rotameter and is universally applicable to gas flow in variable area flow meters.

$$2) \quad F''_i = F' \left(\frac{273}{T} \right) (1 - C_i/2) \quad (17)$$

F''_i = exit gas flow rate, at STP, for gas sample i

C_i = oxygen mole fraction for gas sample i

T = room temperature.

$$3) \quad a. \quad R_i = \frac{F''_i \cdot M(C_i + C_{i+1})}{22,400(0.99W)} \quad (18)$$

R_i = average conversion rate of the sample for the time
between gas injection i and $i + 1$

M = weight of a gram mole of MgO

W = initial sample weight; 0.99 is the MgO purity.

$$b. \quad X_{i+1} = \sum_{i=0}^n R_i (t_{i+1} - t_i) \quad (19)$$

X_{i+1} = total sample conversion at time when gas sample $i + 1$
was injected

t_i = the time that gas sample i was injected, $t_o = 0$ and marks the time the reacted gas first reached the chromatograph.

APPENDIX B.

COMPARISON OF SOME OF THE CHROMATOGRAPH'S

AND TITRATION'S CONVERSION RESULTS .

MgO Powder, 12 cc/min Cl_2

Run #	Temperature	Conversion	
		Chromatograph	Titration
6	563°C	6.8%	7.7%
11	563°C	7.8%	8.2%
14	563°C	8.5%	8.8%
27	690°C	21.5%	22.3%
35 ^a	643°C	51.7%	46.8%

^aMgO powder prepared from $\text{Mg}(\text{OH})_2$.

MgO Powder, 643°C, Reduced Partial Pressures

Run #	Pressure	Conversion	
		Chromatograph	Titration
pp 3	0.46 atm	13.6%	14.5%
pp 4	0.46 atm	12.9%	12.0%
pp 5	0.72 atm	15.4%	14.5%
pp 6	0.72 atm	14.7%	14.0%

MgO Pellets, 643°C

Run #	Cl ₂ flow rate	Conversion	
		Chromatograph	Titration
p 5	10 cc/min	14.3%	15.8%
p 11	10 cc/min	13.4%	14.5%
p 7	40 cc/min	7.7%	7.6%