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KINETICS OF THE HYDROLYSIS OF MgCl_2 AND THE
CHLORINATION OF MAGNESIA

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Kinetics of the hydrolysis of MgCl_2 and
the chlorination of magnesia

by

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NOMENCLATURE

f_i	Fugacity of component i
f_i^o	Fugacity of component i in the standard state
$\hat{f}_i$	Partial fugacity of component i
G	Gibbs free energy
H	Enthalpy
K_A	Equilibrium constant based on activity
K_y	Equilibrium constant based on mole fractions
P	Pressure
Q	Heat input (positive when heat flows into system)
R	Ideal gas constant
S	Entropy
T	Temperature
T_H	Temperature of heat source
T_C	Temperature of heat sink
w	Work (positive when performed by system)
w_s	Work of separation
η	Efficiency factor
ϕ_i	Fugacity coefficient of component i

ABSTRACT*

Two alternatives to the reverse Deacon reaction, $\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons 2\text{HCl} + \frac{1}{2}\text{O}_2$, were examined from thermodynamic and kinetic perspectives.

 MgCl_2 -MgO Cycle MgCl_2 -MgOHCl Cycle

A material balance about either cycle would give product gases common to the reverse Deacon reaction.

The hydrolysis reactions, 1-a and 2-a, were found kinetically feasible although the rates appeared to be diffusion controlled and a function of MgCl_2 preparation. Particle degradation was noticeable for 1-a and attributed to a crystal structure change. Very little particle change was noted for 2-a, likely a result of no change in crystal structure as the valence of the cations did not change.

Chlorination reactions 1-b and 2-b were found to be kinetically more difficult although possible. An attempt to examine the kinetic stability of MgOHCl at higher temperatures in an inert atmosphere was also made.

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INTRODUCTION

One of the more lasting effects of the Arab Oil Embargo and the "energy crisis" has been a realization of the finite amount of fossil and other carbon based fuels on this planet. The result has been a more intensive search for alternative energy sources. Among the sources being examined are geothermal, solar, and nuclear, both fission and fusion. However these energy sources are actually heat sources capable of supplying heat at high temperatures and for many purposes it is desirable to upgrade this energy to a more usable form for the production of work and increased ease in storage and shipping. Currently the transfer of heat from the energy source to water and the ultimate production of electricity has been the only large scale method for upgrading energy. However this process is directly limited by the second law $\left(\frac{w}{Q} = \frac{T_H - T_C}{T_H}\right)$ and the overall efficiency is usually of the order of 20 to 30% (7, 14, 31). due to irreversibilities in the process and the high ambient temperature at the heat sink. Further complicating the scene is that only approximately 20% (10) of the total energy consumed in the United States is electricity although 80% (1) of this total energy is ultimately used for heating purposes. Therefore if these energy sources are to be compatible with our way of life, a method needs to be developed whereby a synthetic fuel or fuels may be produced from these heat sources with characteristics similar to fuels in current use. The decomposition of water with energy obtained at a heat source offers a viable alternative for the production of hydrogen whether to be used as a synthetic fuel or feedstock in making synthetic fuels.

The use of hydrogen as a replacement for natural gas has received careful consideration because the distribution system for natural gas is in place and a switch over would not be extremely difficult although the heating value of hydrogen is about one-third that of natural gas (39, p. 220). In fact a 130 mile hydrogen delivery network has been in operation in Germany for the past thirty years with minimum difficulties (24, pp. 103-104) although it has been estimated that on a per unit energy basis, hydrogen pipeline transmission will cost 30 to 50% more than for natural gas (33). In an attempt to stretch existing natural gas supplies it has been estimated that up to 8% by volume hydrogen may be added to natural gas without requiring equipment alterations. Far term use of hydrogen in the production of carbon based synthetic fuels could require the use of either carbon dioxide (CO_2) or limestone (CaCO_3) as the carbon source. Near term uses would encompass the manufacture of synthetic fuels from coal, tar sands, and oil shale. The potential of using nitrogen chemistry in the production of synthetic nitrogen based fuels such as ammonia (NH_3), hydrazine (N_2H_4), and mixed methyl- and dimethylamines is undergoing careful examination as an alternative due to the ease of obtaining large quantities of nitrogen (24, pp. 52-57).

Worldwide production of hydrogen has increased by three orders of magnitude in the last four decades with one-third of the world hydrogen production in 1973 taking place in the United States. However 93% of the hydrogen produced in the United States has been labeled captive hydrogen which was produced and consumed on-site as opposed to merchant hydrogen made available to the public sector (Figure 1). An examination of current production methods for hydrogen

Figure 1. Distribution of the 8×10^{10} cubic meters (3000 billion cubic feet) of hydrogen consumed in the U.S. in 1973 (24, p. X)

Figure 2. Distribution of energy/feedstock resources for the hydrogen produced in the U.S. in 1973 (24, p. XI)

(Figure 2) indicates fossil fuels to be a common base with natural gas the most desirable (24, p. X-XI). Fossil fuels act both as an energy source and hydrogen donor whereby using methane as an example, one-half of the hydrogen produced originates from methane (CH_4) with the remainder coming from the decomposition of steam. With the shift to higher hydrocarbons or lower hydrogen-carbon ratios, the amount of product originating as water increases. For coal with a hydrogen-carbon ratio of 0.8, 83% of the product hydrogen is water derived (24, pp. 77-80). However, these methods of hydrogen production are in jeopardy because of their reliance on hydrocarbons. An examination of costs, relative efficiency, and energy requirements of alternative methods for hydrogen generation (Table 1) reveals that with current technology, a process does not exist which would compete with fossil fuel hydrogen generation. However as the cost of fossil fuels continue to rise with the ever present possibilities of increased environmental controls, particularly concerning the use of coal, the relative costs should then shift toward the alternatives as technological advances are made.

Government projections through the year 2000 (Figures 3 and 4) strengthens the preceeding logic as hydrogen demand will continue to increase rather dramatically. Major uses of hydrogen will include both the past historical uses and the production of synthetic fuels previously discussed, and will also include applications in the storage of energy at power plants as hydrogen obtained through electrolysis of water during times of nonpeak demand and used at a later time for electrical power peaking generation becomes more common. Also the use of hydrogen as a reducing agent, particularly in iron ore reduction, could easily evolve

Table 1. Relative efficiency and cost of hydrogen production methods
(24, p. XIV)

Primary resource	Cost range \$/GJ	Relative cost	Relative energy requirements
Natural gas (baseline)	0.82-6.59	1.0	1.0
Oil (partial oxidation)	1.55-7.76	1.1-1.9	1.1-1.2
Coal (gasification)	1.26-4.90	0.8-1.5	1.1-1.2
Nuclear (electrolysis)	2.69-32.13	3.3-4.9	2.3-4.8
Solar (20% collection efficiency)	4.76-209	5.8-32	4-6

into a fast growing segment of the "hydrogen economy" (39, p. 285).

Therefore an alternative method for the production of large amounts of hydrogen not reliant on hydrocarbon feedstock does require development and an easily obtainable hydrogen source would be water (H_2O) if a method can be developed to break it into its elements.

The difficulties in decomposing water are reflected in the thermodynamics with a $\Delta G = 285.85$ kJ/g mole and $\Delta H = 237.19$ kJ/g mole at $25^\circ C$ (6). To decompose water thermally would require a temperature of $2000^\circ C$ or greater (32, p. 8; 39, pp. 197-198) and since these conditions are beyond current technology and any expected technological advances in the near future, alternatives need be developed. There are currently three approaches:

1. Electrolysis
2. Closed thermochemical cycles
3. Thermoelectrochemical processes.

Figure 3. Growth in hydrogen demand in the U.S., 1950-2000 (logarithmic plot) (24, p. XII)

Figure 4. Hydrogen projections by use sector, $10^{18} J$ ($10^{15} Btu$) (24, p. XIII)

To provide a common basis of comparison between the alternatives, an efficiency factor (η) is defined as the higher hydrogen heating value divided by the total energy input into the system for decomposition of water. The major difference between electrolysis efficiency as compared to thermochemical efficiency is that all energy for the latter originates as heat at high temperature whereas for electrolysis operating at 25°C, heat equal to $T\Delta S$ or $\Delta G - \Delta H$ (48.66 kJ/g mole) may be theoretically absorbed from the surroundings and not specifically from the heat source. Therefore electrolysis may have an efficiency greater than 100% although the overall efficiency between the heat source and the hydrogen product may be represented by:

$$w = -\Delta G = Q_H \frac{(T_H - T_C)}{T_H}$$

$$\eta = \frac{\Delta H}{Q_H} = \frac{\Delta H}{-\Delta G} \frac{(T_H - T_C)}{T_H}$$

The preceding equations would also be correct for thermochemical cycles if each reaction had no work input, no compression or separation work, and a common upper temperature for the endothermic reactions and lower temperature for the exothermic reactions (31, p. 401).

The first method suggested, electrolysis, has current small scale commercial applications and requires work equal to the negative of the change in Gibbs free energy to be supplied in the form of electrical energy with the remainder of the enthalpy change absorbed from the surroundings. The greatest difficulty in this approach lies not in the actual electrolysis process where efficiencies may soon approach 90%, but rather in the generation of the 237.19 kJ/g mole of electrical

energy to be supplied as work. The efficiency of electrical generation when taking into account the irreversibilities is usually about one-half the Carnot efficiency ($\frac{W}{Q} = \frac{T_H - T_C}{T_H}$) or commonly anywhere from 20 to 33% depending on the upper temperature (31). Higher inlet temperatures reflect higher efficiencies but the efficiency is directly limited by the temperature of the heat sink, T_C , for electrical energy production using steam generators. Since it has been estimated that a 1% increase in efficiency may result in an annual savings of one billion dollars if hydrogen were to replace natural gas and gasoline (23), increasing electrical efficiency is very important. Some experts believe that in the future an upper efficiency of 50% is possible for the overall electrolysis process (32, p. 8).

Because of the rather poor heat to electrical energy conversion, the question as to whether a method could be devised whereby a series of chemical reactions would thermochemically decompose water has been raised. The system as hypothesized would still be subject to Carnot limitations as heat would be absorbed by endothermic reactions at high temperatures and rejected from exothermic reactions at low temperatures. But rather than generating the work required, the work would be produced chemically by the proper sequence of reactions. Regardless of the nature of the reactions or their temperatures or pressures, the overall ΔG , ΔS , and ΔH remain the same as they are state functions. An added advantage of this approach is the possibility of rejecting heat at a considerably lower temperature than is possible in electrical generation resulting in a direct increase in Carnot efficiency. A number of cycles

have since been hypothesized (see Appendix) and many have theoretical efficiencies greater than 50%.

It is conceivable that cycles with higher efficiencies do exist but have not been formulated. However in the theoretical development of the efficiencies, the reactions were usually assumed to run under conditions giving a $\Delta G = 0.0$ for each reaction. By using this approach, the work requirement for running the reaction is zero with all energy requirements being met by adsorption and desorption of heat. Since the majority of the reactions hypothesized fail to go to completion (large equilibrium constant), the energy required to separate the products must be determined. A rough estimate of the heat required for the work of separation may be obtained by assuming ideal work of separation, $W_s = R^*T \sum_{i=1}^m n_i \ln(x_i)$, and dividing by the efficiency of converting heat to work or usually 0.25 to 0.30 (18, 46). Depending on the system, it may be possible to reduce the work of separation by lowering the temperature with proper heat exchange equipment. However the overall approach is subject to error as different separations differ in their degree of nonideality. The efficiency term does not include this added work nor does it include work terms for fluid recycle or transport from vessel to vessel. How these terms will affect the overall process is largely dependent on the number and nature of reactions.

A third alternative would be a combination of chemical reaction with electrolysis whereby the advantages of both approaches would be incorporated into the same water-splitting cycle. A disadvantage would be in the total capital outlay as some equipment common to both approaches

would be required and could be more expensive. Various examples are given in the Appendix.

A true comparison between electrolysis and thermochemical cycles is not feasible at this time due to the large number of unknowns. However a reasonable comparison of efficiencies was reported by Pangborn and Gregory (31). They assumed a heat to work efficiency of one-half the Carnot efficiency for present technology and for futuristic technology, an overall efficiency equivalent to 0.65 to 0.70 of Carnot efficiency. In determining the efficiency of thermochemical cycles, an attempt was made to account for different reaction temperatures, material flow patterns, heat utilization and enthalpy balance as well as calculation of work available from excess heat. Assumptions of perfect heat transfer and negligible work requirements for solid and liquid transfer of reactants and products were made. Further work at the Institute of Gas Technology (39, p. 238) has shown that the final use of the hydrogen produced affects the overall efficiency as hydrogen is particularly well suited for heat production (Table 2).

It would appear that the capital outlay for a thermochemical plant would be a related function of the number of reactions and dependent on the complexity of the reactions and the work of separation. Glandt and Myers (19) claim as a rule of thumb, each additional reaction will require one other major operation. Therefore for a maximum return on investment to be obtained between two competing methods, less total capital investment may be obtained by sacrificing some efficiency. A more thorough examination of the thermochemical cycles in the Appendix would reveal the corrosive nature of many of the materials being handled

Table 2. Comparison of energy-system efficiencies (39, p. 238)

Future system	% efficiency			System efficiency
	Nuclear heat to fuel	Transmission, storage, and distribution	End use	
Hydrogen (95% eff. electrolyzer)	42.8	95	70 (flame)	29
			84 (catalytic)	34
Electricity	45	90	95	38
Hydrogen (thermo-chemical)	55	95	70 (flame)	37
			84 (catalytic)	44

resulting in increased initial costs, increased maintenance costs, and possibly a shorter life expectancy for the plant, all affecting the return on investment.

The upper temperature of the endothermic reactions will also be a factor in the matching of thermochemical cycles to heat sources as the degradation of any heat to a lower temperature will decrease the overall efficiency. Therefore it would appear that rather than develop one cycle, a series of cycles, each applicable to a given temperature range need to be developed (24, p. 87). Another work term excluded in determining the efficiencies of electrolysis and thermochemical cycles is the compression of the hydrogen product to an adequate pressure for transportation and storage. Westinghouse (16, pp. 3-7) argues that the work term may be added directly in the electrolysis operation by operating at the desired outlet pressure as opposed to redesigning

and building expensive compressors and providing compression work for thermochemical cycles. In fact it has been shown that electrolysis cells work more efficiently at higher pressures and that the gain in efficiency usually more than offsets the increase in electrical energy required (39, p. 28).

An attempt is not being made by the author to downplay thermochemical cycles but rather an objective presentation of potential difficulties. There are numerous problems but electrolysis is currently operating at only 20 to 30% efficiency so there is room for problem solving in an alternative process even at the risk of some loss in overall efficiency. The possibility does exist that electrical generating efficiencies may some day approach 50% resulting in an overall electrolysis efficiency of approximately that. However this may be wishful thinking, and, if possible, the capital outlay may be quite large. Therefore any in-depth comparison between the two approaches or a combination of the two is at this time very difficult at best and more facts (less opinions) are needed before a qualitative judgment may be made. In the end, economics will dictate which is feasible but for the time being, good objective data must be obtained and made available to the scientific public.

LITERATURE REVIEW

The thermochemical cycles in the Appendix are grouped under one of four headings as suggested by Chao (7).

- 1) Halide Processes
- 2) Reverse Deacon Processes
- 3) Iron Oxide and Carbon Oxide Processes
- 4) Metal and Alkali Metal Processes.

However of particular interest to this researcher are those cycles which employ the Reverse Deacon reaction.

All thermochemical cycles possess three unique steps according to Abraham and Schreiner (2): water binding, product recovery, and reagent regeneration. The uniqueness of the Reverse Deacon in the hypothesizing of thermochemical cycles is characterized by its containing both the water binding and oxygen recovery steps. However with this inherent advantage, there are added difficulties in the separation of the four gaseous components. An examination of the equilibrium mixture for stoichiometric feedrates (Figure 5) reveals that high temperatures favor product formation, but the approach to complete or nearly complete conversion is virtually impossible at the available temperatures. Therefore the system has four gaseous components which must be separated and two of them recycled back to the feedstream. It would be desirable to reduce the ideal work of separation, $W_s = R^*T \sum_{i=1}^m n_i \ln(x_i)$, by cooling the mixture to a lower temperature but the reaction may require

Figure 5. Reverse Deacon reaction; conversion as a function of temperature. (Stoichiometric feed of reactants, total pressure 1 atmosphere.)

rapid quenching in a highly irreversible manner to a temperature at which the kinetics would not favor a shift back toward equilibrium and the formation of reactants in the time-span required for separation. A general procedure for the separation of the four components would be to quench the reaction resulting in the condensation of a $\text{H}_2\text{O}-\text{HCl}$ mixture which would then be distilled. The distillation requires an azeotrope breaker unless an azeotropic mixture can be used as a feed-stream. The separation of Cl_2-O_2 mixture would then be performed by cryogenically cooling until chlorine condenses. An alternative to this approach particularly applicable to small amounts of chlorine in oxygen would be to use a chlorine absorbent such as sulfur monochloride. The chlorine would then be stripped upon heating (46).

The data for the equilibrium diagram (5) previously cited was obtained by assuming an ideal solution and upon examination of the $\frac{f_i}{p}$ term obtained from generalized compressibility charts (22, pp. 601-604), it was found that at one atmosphere the term was approximately one for all gases.

$$\Delta G = - RT \ln K_A$$

$$K_A = K_\phi K_y p^\nu$$

$$\phi_i = \frac{f_i}{p} \quad (\text{ideal solution})$$

$$K_A = K_{f/p} K_y p^\nu$$

$$\frac{f_i}{p} \approx 1 \quad (\text{at } p = 1 \text{ atm})$$

$$K_A = K_y \quad (\text{at } p = 1 \text{ atm})$$

The results were confirmed by the author using thermodynamic data from Barin and Knacke (6, pp. 219, 319, 323, 584).

From the equilibrium diagram, it would then appear desirable to run the reaction at the highest temperature readily feasible so as to have maximum equilibrium conversion, a more kinetically favored reaction, and minimum recycle work. However work performed by Yeh (50, pp. 36-37) indicated that in the temperature range of 950°K with near stoichiometric feed and a residence time of 6 sec., only 22% chlorine conversion of an expected 56% conversion at equilibrium was obtained. It would then be desirable to have or to develop a catalyst capable of withstanding the corrosive environment and high temperatures giving a reduced activation energy and a more kinetically favored reaction. However the discovery of such a catalyst has not been noted although CuCl_2 may be acceptable up to 500°C (32, p. 15) before decomposing. There have also been various accounts of using CaCl_2 , BaCl_2 , MgCl_2 , and NiCl_2 to catalyze the reactions but each appears to be subject to difficulties such as the high vapor pressure of the catalyst at the temperature desired (37, pp. 412-413). Complete conversion of chlorine has been achieved by using a nonstoichiometric 4 to 1 water to chlorine ratio in the feedstream, but increased work requirements for the $\text{HCl-H}_2\text{O}$ separation makes this approach of doubtful utility (27).

Because of the various difficulties inherent to the Reverse Deacon reaction, a search for a suitable alternative has resulted in three potential solutions employing magnesium chemistry and heterogeneous reactions.

I (48)

II (32)

III (2)

The overall balance of any of the above pairs is the Reverse Deacon reaction.

The first alternative has been examined rather extensively by Powers (32, pp. 62-69). Reaction I-b is run in an aqueous solution and extraction of crystalline $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ product requires considerable energy due to the heats of hydration.

The second and third processes employ solid-gas heterogeneous reactions in both steps in an attempt to avoid some of the difficulties of the homogeneous Reverse Deacon reaction or magnesium chloride in aqueous solution. Either process as suggested could employ a fixed bed

reactor whereby reaction (a) and (b) would be run in an alternating pattern (Figure 6) by introducing the appropriate feedstream. A comparison between process II and III reveals only one major difference, reaction pair II attempts to stop the $\text{MgCl}_2 \rightarrow \text{MgO}$ hydrolysis reaction at the MgOHCl intermediate which may be stable depending on both the kinetics and partial pressure of HCl maintained.

Equilibrium product concentration of HCl and O_2 are given in Figures 7 and 8 for reaction pairs II and III. Similar assumptions were made as for the Reverse Deacon equilibrium diagram plus the $\frac{f_i}{f_i}$ or activity term for the solids was assumed to be one which introduced negligible error due to the choice of standard states (6, pp. 437, 441-442). The hydrolysis and chlorination reactions are drastically different as the hydrolysis reaction for II is exothermic whereas for III it is endothermic and vice-versa for the chlorination reaction. It is usually advantageous in thermochemical cycles to have the high temperature reaction endothermic thereby having the potential to obtain maximum chemical work as is the case for reaction pairs II and III. It would appear that II would be the more efficient due to its ability to give up heat to the environment at 227°C as suggested by Schulten et al. (35).

The hydrolysis reactions, II-a and III-a, have been examined experimentally and appear to be kinetically feasible. Schulten and associates (35) have confirmed the MgCl_2 hydrolysis to MgOHCl as essentially complete at 227°C although no kinetic parameters were given. da Cunha (11) has examined reaction III-a, hydrolysis to MgO , at 600°C and noted conversion of 72 to 97% with a solid residence time of 60 to 70 min. (Figures 9, 10, and 11). The final conversion appears to be a

Figure 6. Reaction system using fixed beds of magnesium compounds

Figure 7. Equilibrium diagram for hydrolysis reactions II-a and III-a

Figure 8. Equilibrium diagram for chlorination reactions II-b and III-b

Figure 9. Course of the nondecomposed MgCl_2 fraction as a function of time (+ 14 mesh) (11)

Figure 10. Course of the undecomposed MgCl_2 fraction as a function of time (- 14 + 28 mesh) (11)

Figure 11. Course of the undecomposed MgCl_2 fraction as a function of time (- 28 mesh) (11)

function of initial particle size with the large particle runs possibly showing diffusion effects as complete conversion was approached.

Unfortunately no data were given on the flow rates of steam and argon or the outlet concentration with which approach to equilibrium calculations could have been made. Similar work at Ames Laboratory by a summer trainee (15) paralleled da Cunha's work.

The chlorination reactions, II-b and III-b, appear to be very questionable and will require individual examination. There are some very perplexing problems concerning the MgOHCl intermediate, largely of a kinetic nature and undeterminable without experimental data. Table 3 gives the equilibrium partial pressures of HCl required to prevent MgO formation as calculated thermodynamically by Kelley (26), but Forrester (17, pp. 10-14) has determined MgOHCl to be stable up to 350°C with no information readily available as to an uppermost temperature of kinetic stability. The difficulties with reaction II-b are threefold: first an HCl partial pressure must be maintained to prevent MgOHCl decomposition if kinetically favored; second, the reactivity of the MgOHCl is unknown; and third, water is given off as a product and may react by II-a giving a final mixture similar to the Reverse Deacon (H_2O , Cl_2 , HCl , and O_2). In fact work performed by Schulten and associates (35) at temperatures where the MgOHCl is stable failed to produce any oxygen when chlorination was attempted. However when chlorine and water were fed into the system, oxygen was evolved at temperatures as low as 135°C . This may help to explain and confirm the mechanism and catalytic effect of MgCl_2 - MgO mixtures on the Reverse Deacon reaction noted and hypothesized in 1934 (37). In any

Table 3. Conversion of MgOHCl to MgO at high temperature (26). Reaction:
 $\text{MgOHCl} \rightleftharpoons \text{MgO} + \text{HCl}$

Temperature °K	Equilibrium vapor pressure of HCl , atmospheres
298	2.80×10^{-12}
400	1.30×10^{-7}
500	6.68×10^{-5}
600	4.27×10^{-3}
700	7.36×10^{-2}
800	6.12×10^{-1}
828	1.00

event the applicability of reaction pair II as hypothesized by Schulten may be extremely questionable if at all possible.

The chlorination of MgO appears to be difficult as the reactivity of MgO is not thoroughly understood and in many instances has the attributes of an art as opposed to a science. Trends in the preparation of MgO have shown the resulting reactivity to be a function of both the temperature of preparation and the time at that temperature. Chown and Deacon (9) in examining the reactivity of MgO with respect to hydration to magnesium hydroxide ($\text{Mg}(\text{OH})_2$) also noted the reactivity to be a function of temperature but chose to take their investigation one step further. Their results indicated the activity to be a function of total surface area and directly related to the pore structure as larger pores were proven to exist at lower temperatures of preparation giving a more active MgO . This seems to correlate with work performed by the

Bureau of Mines (13) where MgO was chlorinated using carbon monoxide (CO) as a reducing agent. They noted a 370% increase in volume in going from the oxide to the chloride and found the center of the particles to be as well chlorinated as the outer surface. They did observe the MgCl_2 formed to be a hard dense solid which rapidly filled the pores on the surface forcing the reaction to stop. By placing the MgO in an inert porous bed (dolomite), conversion was increased rather dramatically. This was attributed to the ability of MgCl_2 product to expand in the inert bed and appears to contradict their earlier conclusion, which was that the reaction stopped because the pores of the particles were sealed. However it could be that part of the increase in yield resulted from sharper temperature gradients around the reacting particles and better removal of the exothermic heat of reaction ($\Delta H = 24.55$ kJ/g mole at 523°C). They did state that a sizable increase in volume of MgCl_2 occurred when melted to a liquid (which occurs at 707°C (20, p. B106)) and possibly this could stop the reaction as the liquid flows outward toward the particle surface, cools, and solidifies thus filling the outer pores. It should be noted that only one crystal structure exists for either MgO (cubic) or MgCl_2 (hexagonal) in the temperature range of concern (20, pp, B105-106). The preceding work was performed using CO as a reducing agent which made the reaction more kinetically favored and very little work on the direct chlorination of MgO has been found. Initial work performed at Ames Laboratory (25) indicated a rapid initial rate followed by a very slow reaction with an overall conversion of 4 to 9.5% in the 550 to 650°C temperature range on MgO prepared from $\text{Mg}(\text{OH})_2$.

PREPARATION OF ANHYDROUS MgCl_2

One of the major difficulties was the preparation of anhydrous MgCl_2 on the bench scale. Numerous patents have been issued on the topic (4) and in most instances, the conditions required are very difficult to maintain on the bench scale. Ninety-eight percent anhydrous MgCl_2 is available from Apache Chemicals, but for hydrolysis work the remaining 2 weight percent of water must be removed as it corresponds to an average of 1/10 water molecule per MgCl_2 or 10% of the water required for the hydrolysis reaction. 99.999% anhydrous MgCl_2 is commercially available but was judged too expensive for preliminary kinetic work.

Kelley in his thermodynamic analysis of MgCl_2 cited the requirements for dehydration of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ to MgCl_2 . Upper temperature limits were given at which the hydrated salt would form a saturated solution and these conditions were avoided (26). Very little kinetic data on the rates of side reactions or the removal of hydrated water was found. However the removal of the last two molecules of water was performed under an HCl atmosphere as MgOHCl or MgO could be formed although rates of formation of either as a function of temperature were not found. No doubt some MgOHCl may be formed in removal of the first four waters but may be converted back to MgCl_2 under the HCl atmosphere.

Initial dehydration work paralleled Kelley's suggestions except all waters of hydration were removed under an HCl atmosphere. Because the dehydration was expensive and time consuming, only small amounts of MgCl_2 could be produced. Eventually

it was noted there were variations in different jars of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ as obtained from the manufacturer which affected the rate and way in which the waters of hydration were removed. These variations appeared to be largely a result of storage as bottles of the same lot number and analysis contained MgCl_2 of varying degrees of hydration and various particle agglomerations. Therefore any attempt to close a mass balance about the $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ dehydration to MgCl_2 was fruitless as the starting material may or may not have exactly six waters per MgCl_2 molecule. To get a uniform starting material the $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ with a solubility of 367 g/ml in hot water was dissolved in hot water and then cooled in an ice bath to decrease the solubility to 167 g/100 ml (20, p. B106). This resulted in the rapid formation of needle-like crystals. The solution was then filtered with a slight vacuum and the liquor reheated whereby more $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ would be added and the process repeated. The crystals were placed in their original jars, weighed, sealed, and stored for future dehydration work.

Allen and Clark (3) prepared anhydrous MgCl_2 for their work using a method developed by Manocha and Sternheim (29). The uniqueness of the technique developed by Manocha and Sternheim was that 4 out of the 6 waters of hydration could be safely removed outside an HCl environment with the remaining two waters removed in a 10 to 11 hour process.

This was particularly well suited for preparation of MgCl_2 for our work as ovens were readily available for removal of the first 4 waters and HCl lecture bottles could be used for maintaining an HCl atmosphere during removal of the last 2 waters of hydration. The

procedure used for MgCl_2 preparation was not identical to that of Manocha and Sternheim although the approach was quite similar.

1) Place the $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in an open container and place in an oven at 80°C . The mixture must be frequently stirred to prevent sintering of particles. When the particles fail to sinter usually after a weight loss of 5 percent, this step is completed.

2) Raise the oven temperature to 95°C and maintain till water loss is to $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$ assuming the starting material to be $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.

3) Raise the oven to 135°C and maintain until $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ is approached but do not lose more than 4 waters per MgCl_2 molecule.

4) Place under an HCl atmosphere with a small flow rate of dry HCl and raise the temperature to 250°C and maintain until approximately 70% of the remaining water is removed.

5) Gradually raise the temperature (1°C per min.) up to 305°C and maintain until little vapor condenses out of the exiting HCl stream.

6) Raise the temperature to 350 to 375°C and maintain until no water is condensed.

7) Store in a tightly sealed container and place in a desiccator if possible.

For experimental use, the anhydrous MgCl_2 was screened inside a dry box and sealed again in containers. The particle size distribution was:

<u>Mesh size</u>	<u>Percent</u>
+ 6	≈ 0%
- 6 to + 16	31%
- 16 to + 200	69%
- 200	≈ 0%

Of particular importance were the particles in the - 16 to + 200 mesh size as they were quite uniform in shape and size. The particles in the next larger size grouping appeared to be composed of particles of approximately the same shape and size but fused or sintered together and were fairly fragile.

Final preparation of MgCl_2 before a hydrolysis run consisted of loading the particles in the reactor in the open air being careful not to touch or breathe on the particles and placing the reactor in the furnace with a small flow rate of HCl . The furnace was turned on to give a temperature of 410°C in the reactor zone which was reached after 15 to 20 min. and after a total of 45 min., the temperature was raised to 430°C for 15 min. The particles darkened in color from a brilliant to dull white with a small but noticeable amount of water condensing out of the exit HCl stream. The MgCl_2 bed weight usually decreased by less than 1% giving a final composition determined analytically of essentially 100% MgCl_2 .

EQUIPMENT DESIGN

Since the majority of the experimental work was to center about reaction pair III and this being the first work of this nature performed in the group, design and construction of new equipment and the purchase of other equipment was required.

Initially it was felt that III-a would be the more difficult reaction and equipment was designed primarily for it and then adjusted to meet the requirements for III-b.

Since reaction III-a required a small continuous flow rate of steam under precise control, a syringe pump was purchased to pump liquid water which was then vaporized. A sketch of the steam generator is shown in Figure 12. The syringe pump chosen was a Sage Instrument Model 355 with a continuous flow rate range of 0.000058 ml/hr to 140 ml/min depending on the syringe size and percent flow selected. B-D Multifit syringes with the Luer-Lok Tip were chosen as they met the syringe pump manufacturer's specifications for calibration plus the Luer-Lok Tip provided an excellent method of connecting the syringe to the steam generator with no leakage when a small amount of vacuum grease was applied about the connection. The end of a needle was cut off with the male base welded to 1/4" stainless steel tubing which was then encased in a graphite block with the exit end welded to a Kovar to glass joint. The glass section possessed a socket joint for connection to the reactor vessel. The graphite block was wrapped with furnace wire (resistance

Figure 12. Steam generator

of 1.6 ohm/ft) to give an overall resistance of 20 ohm with a stainless steel band placed around the furnace wire to hold it in place. The steam generator was then wrapped with insulation and placed in a container. A hole drilled in the graphite block permitted a thermocouple to be inserted for temperature monitoring. A current of 2.1 amps was sufficient to maintain the generator at 300°C.

Regions where the steam flow rate would become unstable were noticable and appeared to be dependent on several factors such as: the steam generator temperature, the temperature of the syringe and syringe connection, and primarily the water flow rate into the steam generator. Instability was readily noticed by the pulsating of vapor caused by the instantaneous vaporization of water droplets which must be avoided. An improved steam generator would involve turning the present generator on its side and tilting at a 15° angle to reduce the tendency to form droplets. For our purpose, the steam flow rates over the region of interest were quite stable with the initial steam generator design.

The construction of a reactor vessel presented considerable difficulty as it was desirable to use quartz over that portion of the reactor subject to high temperatures. Therefore some method of supporting the bed required development and a search for a porous quartz plate initially failed. The possibility of using quartz plates with holes drilled by diamond bits was examined and considered impractical due to particle and hole size. Attempts to cement porous alundum into vycor tubing capable of withstanding the upper temperatures also failed because of the unfavorable coefficient of expansion which caused the vycor to crack.

upon heating. Another effort was then made to find a porous quartz plate with numerous inquiries mailed. Eventually both a porous quartz plate and a quartz cloth were found. Tissuquartz 2500 QAST, a high temperature quartz cloth manufactured by Pall, was finally chosen as it could be ordered in the desired size and placed on quartz plates with holes drilled in them. The pressure drop would be considerably less than for a porous quartz plate and the cloth could be used to separate the bed of particles into separate zones enabling one to stop the reaction and analyze each zone. The final design of the 8 mm diameter reactor is shown in Figure 13. One unique feature of the 8 mm reactor is that the base of the bed is supported by quartz cloth placed on 5 mm quartz tubing allowing the base to be adjusted. This will become increasingly important when temperature profiles within the reactor are discussed. The design of the 24 mm diameter reactor is quite similar except a quartz plate with holes was fused into the reactor and the quartz cloth laid on top. The bed height could not be easily adjusted. The 8 mm diameter reactor was used primarily for kinetic investigations with the 24 mm used for runs requiring a large amount of solids. Each reactor contained a region of quartz chips designed to smooth out any fluctuations in steam flow and provide better heat transfer in the preheater zone of the reactor. The exiting gas was then routed to the appropriate vessel for analysis. The analytical technique is discussed in a later section.

The furnace used for heating the reactor to operating temperature was a Lindberg Model 54341 Tube Furnace placed in a vertical position coupled with a Lindberg Solid State Digital Controller Type 2200 capable of control setability of $\pm \frac{1}{2}^{\circ}\text{C}$ and an accuracy of $\pm 1^{\circ}\text{C}$. Although the

Figure 13. 8 mm reactor vessel

furnace was capable of excellent temperature control and reproducibility, it was desirable to determine the temperature profile through the reaction zone under conditions similar to both a hydrolysis and chlorination runs. The effect of placing the furnace in a vertical position became readily apparent and to obtain the desired temperature profile, insulating plugs constructed of firebrick (insulating brick) were made and inserted into the ends of the furnace to prevent airflow. An in-depth examination of the problem is made in the Experimental Work section.

Heating tape over asbestos cloth was used on open surfaces for the hydrolysis reaction as required to prevent condensation. A silicon-based vacuum grease was used on all joints and stopcocks and withstood the upper temperatures and corrosive environment reasonably well. Ball and socket joints were used as often as possible when joints were required to avoid problems associated with joints freezing at high temperatures. The ball and socket joint provided a tight fit when clamped together and a small amount of silicon-based vacuum grease was usually applied. Standard tapered joints were required on the reactor and did occasionally provide some problems which were eliminated by application of vacuum grease and the periodic turning of the joint when at high temperatures.

The equipment required very little alteration when a chlorination run was made as can be seen in Figures 14 and 15. Chlorine was obtained from a cylinder and the flow rate monitored by a Brooks chlorine rotameter and dried by passing through CaCl_2 . The chlorine gas then passed through the reactor with flexible Teflon tubing used to route the product gas to the appropriate vessel for analysis.

Figure 14. Experimental apparatus layout for a hydrolysis run

Figure 15. Experimental apparatus layout for a chlorination run

Figure 16. Experimental equipment for hydrolysis run

Mass Balance about the Reactor

Any kinetic investigation requires methods of completing a mass balance about the system before experimental data may be thoroughly evaluated and models hypothesized. The experimental work for the heterogeneous reactions studied required a determination of entering and exiting gas compositions and mole flow rates and also a procedure for determining the composition of the solids undergoing reaction.

Methods for determining the bed composition were identical for either the hydrolysis or chlorination reaction. Russian scientists and engineers (38, 47) have performed considerable work in the fields of $\text{MgCl}_2\text{-MgO-H}_2\text{O}$ cements and have developed and confirmed experimentally methods for determining Mg^{+2} , Cl^- , and combined OH^- and O^{-2} content. Smirnov and fellow workers (38) found that by dissolving the sample in nitric acid (HNO_3), the combined O^{-2} and OH^- content could be determined by back titration and then by adjusting the pH to 8.5 and using Mohr's method, the Cl^- content could be determined. It was noted that it made no difference whether the above operations were performed on the same or separate samples. The Mg^{+2} content was then determined by using Trilon B and Chrome Dark Blue indicator. Schulten and associates (35) when performing experimental work on $\text{MgCl}_2\cdot\text{H}_2\text{O}$ and mixture of MgCl_2 , H_2O , and MgOHCl , found the preceding methods for Cl^- and combined OH^- and O^{-2} determination to be acceptable but choose to determine Mg^{+2} content complexometrically using EDTA as the complexing agent and Eriochrome Black T as an indicator. For our work, the technique suggested by Schulten was used.

Determination of Solids Content

Weighed samples (approximately 1 g) were dissolved in a minimum amount of HNO_3 and it was found that when using 0.4 M HNO_3 , approximately 125 ml of liquid was required to dissolve 1 g MgO and 62.5 ml to dissolve 1 g MgOHCl . The solution was then diluted by filling the remainder of either a 200 or 100 ml volumetric flask respectively with distilled water. Some difficulty was noted in getting the solid to go into solution as it was not instantaneous.

Analysis for Cl^- was made by using Mohr's titration (12) with 0.1 M silver nitrate (AgNO_3) and using sodium chromate (NaCrO_4) as an indicator. Excess acid in the aliquot was neutralized with calcium carbonate (CaCO_3) and the yellow mixture was then titrated with AgNO_3 which in the presence of Cl^- formed silver chloride (AgCl). The absence of free Cl^- in the solution was noted by the formation of a red precipitant, silver chromate (Ag_2CrO_4).

The OH^- and O^{2-} content were determined by back titration of the excess acid used for dissolving purposes. Sodium hydroxide (NaOH) was used for titration with phenolphthalein as an indicator. When using HNO_3 as the dissolving acid, one equivalent HNO_3 would react with one equivalent of OH^- in MgOHCl and one-half mole O^{2-} as in MgO .

Mg^{+2} was determined by complexometric titration of the solution with EDTA using Eriochrome Black T as an indicator (34, pp. 83-87; 36, pp. 62-63). The solution was initially buffered to a pH of 10 and the endpoint noted by a change in color from red to blue. The complex formed in a one to one Mg^{+2} to EDTA ratio. The buffer was prepared

by dissolving 70 gr ammonium chloride (NH_4Cl) in 285 ml of ammonium hydroxide (NH_4OH) with a specific gravity of 0.899 and the solution was then diluted to one liter.

Although the analytical results are sufficient for determining composition of a two component mixture consisting of either MgCl_2 , MgOHCl , MgO , and H_2O , initial weight data is required for determining the composition of a three component system. For a four component system there are five unknowns, Mg^{+2} , Cl^- , O^{-2} , OH^- , and H_2O , and only four independent equations or measurements. They are Mg^{+2} , Cl^- , and combined OH^- and O^{-2} mole numbers and the total weight of the sample. However in most situations one of the unknowns may be eliminated such as H_2O content at high temperatures or OH^- mole number at temperatures beyond the kinetic stability of MgOHCl without introducing sizable error.

Determination of Gas Compositions and Flow Rates

For the hydrolysis reaction, the steam flow rate into the reactor was controlled by the syringe pump with reasonable accuracy. The exiting H_2O - HCl mixture from the reactor was then bubbled through a porous plate into slightly basic water and titrated with NaOH using phenolphthalein as an indicator. Passing the gas through a porous plate resulted in better gas-water contact and total HCl absorption with the temperature of the titration flask being maintained by an ice bath. The titration process was semicontinuous, that being 1 ml of NaOH solution was added to the titration flask and the time of color change would be monitored. No solution was ever removed from the flask so cumulative errors

from earlier titrations could not propagate or each color change was independent of the previous one and only dependent on the total amount of NaOH and HCl which had gone into the solution. By knowledge of the inlet feed rate of steam and the outlet flow rate of HCl (barring large diffusion effects which did not seem to be the case) and the fact that each water which reacted would produce two HCl molecules, the exit composition could be determined.

The gas flow rates and compositions for the chlorination reaction were more difficult to determine since the components were chlorine and oxygen and each chlorine molecule (Cl_2) which reacted would produce only one-half of an oxygen molecule ($\frac{1}{2} \text{O}_2$). The chlorine flow rate was regulated by using a chlorine rotameter, but determination of the rate at which oxygen was evolved proved to be more difficult. It was decided that oxygen evolution would be determined by bubbling the exit gas through a potassium iodide (KI) solution which would absorb the chlorine by the following mechanism (49, p. 371).

The exiting oxygen evolution would then be measured by volumetric displacement of the KI solution in an inverted graduated cylinder. However at the start of an experimental chlorination run there would be some gas in the system and if it were not absorbed by the KI solution, determination of the evolution rate of oxygen would be in jeopardy. Therefore HCl gas was chosen to occupy the system at the start of a

run which would be absorbed by the KI solution due to the high solubility of HCl in water. Outlet concentrations could then be determined.

Ideally a gas chromatograph would be used to determine O_2-Cl_2 concentrations with far better accuracy than obtainable from the above method.

EXPERIMENTAL WORK

Experimental work consisted of making the experimental equipment operational and preliminary kinetic examinations of the MgCl_2 - MgO and MgCl_2 - MgOHCl cycles.

Temperature Profiles

One of the problems encountered in making the equipment operational was obtaining acceptable temperature profiles over the reaction zone of the reactor. Although the furnace was designed by the manufacturer to give a reasonably constant temperature profile over the middle one-third of the furnace when in a horizontal position, placing the furnace in a vertical position totally disrupted the profile as convection currents caused by the warmer air rising out of the furnace developed. As may be seen in Figure 17, a temperature variance of 70°C over an 11-inch reaction zone was present in initial runs. Attempts were made to obtain a more uniform temperature profile by plugging the lower, upper, and both ends of the furnace with various materials to restrict air flow. Finally, an attempt was made to eliminate all air flow into the furnace and rely on radiant heat transfer and convection inside the furnace. Plugs constructed of firebrick were made and provided a reasonably tight fit at the top and bottom and extended into the furnace to the same depth as the furnace insulation. The temperature profiles obtained were quite adequate for the anticipated use as a variance of only 7 to 13°C over a 6-inch zone was found. Deviations in temperature profiles under hydrolysis conditions as opposed to no gas flow were

Figure 17. Initial temperature profile for 600°C setpoint

found to be small and usually of the order of several degrees. Therefore it was felt that any deviation in temperature profile caused by a small chlorine flow rate (15 cc/min at 25°C) would be negligible. As may be seen in Figures 18-24, the setpoint temperature of the controller did not match the average temperature in the reaction zone except at high temperature. By knowledge of the temperature profiles and setpoints over a number of temperatures, extrapolation to other temperatures and setpoints was possible.

The temperature profiles were obtained by extending a chromel-alumel thermocouple to various depths in the reactor at which the potential would be read by a potentiometer. After various corrections to the potential reading, the temperature would then be read from a standard table for chromel-alumel thermocouples.

MgCl_2 -MgO Cycle

The hydrolysis reaction of converting MgCl_2 to MgO was examined in an attempt to determine the controlling mechanism and other desirable observations. Although numerous runs were made, reproducible data was difficult to obtain though various trends were readily noticed. The difficulty in obtaining reproducible data may be attributed to a number of factors, some related to the experimental equipment and others associated with heterogeneous reactions. Any attempt to separate the effects of these variables on the experimental results was very difficult. Factors affecting reproducibility were:

Figure 18. Temperature profile for 238°C setpoint

Figure 19. Temperature profile for 365°C setpoint

Figure 20. Temperature profile for 472°C setpoint

Figure 21. Temperature profile for 550°C setpoint

Figure 22. Temperature profile for 600°C

Figure 23. Temperature profile for 650°C

Figure 24. Temperature profile for 695°C setpoint

- 1) Determination of small steam leaks about the stopcocks and joints was very difficult because of the presence of heating tape.
- 2) The condensation of steam as it entered the titration flask created a small vacuum which increased as the amount of unreacted steam increased.
- 3) Particle alignment within the bed was strictly by chance and could easily affect steam distribution.
- 4) Although new quartz cloth was used on each run to support the bed, the steam distribution through the cloth was questionable and da Cunha (11) noted rates to fluctuate upon changing the bed support (porous plate).
- 5) Fluidization and particle degradation did occur to varying degrees as the MgCl_2 was converted to MgO . The particle degradation appeared to be a function of the MgCl_2 heat treatment history, particle size, and crystal structure change.

In order to determine the controlling mechanisms for the reaction, a steam flow rate was required which would not approach equilibrium concentrations when passed through the bed. A flow rate of 6 ml/hr of water was normally used which resulted in the following steam flow rates through the 8 mm reactor at the given temperatures (21, p. 429).

<u>Temperature</u>	<u>Volumetric flow</u>	<u>Velocity with no bed</u>
695°C	71.54 cm ³ /sec	142.32 cm/sec
570°C	63.78	126.89

To prevent bed fluidization and removal of particles from the reaction zone, quartz cloth was laid on the MgCl_2 bed with a piece of 5 mm quartz

tubing placed on top. The tubing was held in place by a bend in the reactor.

The majority of the experimental work was performed on -16 to +200 mesh MgCl_2 which was prepared as cited in a previous section and exceptions will be noted. The average run contained 5 g of MgCl_2 with an error in weighing of ± 0.1 g. Upon 100% conversion, approximately 0.10 g mole of HCl would be evolved. The material of known heat treatment showed very little particle degradation due to fluidization within the bed during the hydrolysis reaction although the bed did shrink by 25% causing gaps and cracks to form. A small amount of powder and smaller particles was noted between gaps indicating some fluidization but the amount was usually a very small portion of the total bed. The similarity in MgCl_2 particles in the -16 to +200 mesh range is shown in Figure 25 and most likely is a result of crystal growth in the recrystallization process. The change in shape and particle size of the MgO product becomes apparent in Figure 26 as some degradation has occurred and may be partially attributed to crystal structure transformation (hexagonal to cubic).

A very distinctive trend noted on practically all runs was the linear conversion of MgCl_2 to MgO over a large mole fraction range. Examination of Figure 27, one of the initial runs, demonstrates the linear region of conversion. However an examination of the temperature profile for this particular run (Figure 17) would indicate a variance of 70°C . Other experimental data will demonstrate the same trend although the temperature variance within the reaction zone has been reduced to approximately 10°C .

Figure 25. -16 to + 200 mesh MgCl_2 particles

Figure 26. MgO product of -16 to + 200 mesh MgCl_2 after hydrolysis reaction

Figure 27. Linear rate of $\text{MgCl}_2 \rightarrow \text{MgO}$ hydrolysis with a 70°C variance in the bed

Final conversions varied but 90 to 100% conversion was common with essentially 100% conversion being confirmed from either HCl evolution or analytical determination of the solid product.

Data obtained from hydrolysis runs at various temperatures are presented in Figure 28 where temperature would appear to have negligible effect on rates. Deviation at the start of a run may be attributed to inert (argon) within the system. The lack of rate dependency on temperature would indicate diffusion to be a likely controlling factor. Data at 570 and 695°C obtained under conditions identical to those in Figure 28 are shown in Figure 29. At both temperatures, rates have increased considerably and were reproducible (Figures 30 and 31). The results of Figure 29 are as would be expected if diffusion were controlling. The linear portion of the rate has increased by a factor of 1.16 with a 125°C change in temperature. The maximum exit composition of the 570°C run contained 48.7 mole % HCl compared to an equilibrium value of 67.8%. For the 695°C a composition of 56.6% HCl was determined in the outlet stream as compared to an equilibrium value of 86.5%. Steam residence time in the bed was considerably less than 0.1 sec and probably of the order of 0.05 sec. Effects of approaching equilibrium are questionable, particularly when most models impose the assumption that gas composition does not change appreciably. Data as in Figure 28 cannot be disregarded due to the many variables in heterogeneous reactions; particularly steam distribution and channeling within the shrinking bed.

Although the MgCl_2 material used for the previous work had been obtained from $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ recrystallized out of solution, a considerable

Figure 28. Experimental data of $\text{MgCl}_2 \rightarrow \text{MgO}$ hydrolysis

Figure 29. Experimental data of $\text{MgCl}_2 \rightarrow \text{MgO}$ hydrolysis

Figure 30. $\text{MgCl}_2 \rightarrow \text{MgO}$ hydrolysis reproducibility at $\approx 570^\circ\text{C}$

Figure 31. $\text{MgCl}_2 \rightarrow \text{MgO}$ hydrolysis reproducibility at $\approx 695^\circ\text{C}$

amount of anhydrous MgCl_2 was made before the recrystallization method was adopted as little deviation was noted in initial shipments of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. However upon drying to MgCl_2 , the density of that which had been recrystallized was approximately 0.647 gr/cm^3 as compared to 0.415 gr/cm^3 for that which had not been. The latter MgCl_2 upon hydrolysis showed the distinctive property of particle degradation to a powder as higher conversions were approached. The reason for the particle breakdown is not readily apparent but may be related to the lower density and previous heat treatment. A comparison of hydrolysis rates of MgCl_2 of different heat treatments is shown in Figure 32. The initial linear rate is similar to that in previous hydrolysis work with the sudden increase in rate due to the particles breaking down to an extremely fine powder and the effect of diffusion resistance being drastically reduced. Kinetic work and modeling on the above material would be difficult as high steam flow rates would be required to avoid approaching equilibrium concentrations due to the formation of the powder. The degree of fluidization of the powder is questionable due to the small reactor size and the steam flow rates and attempts to apply fluidized bed models would be difficult and most likely not applicable.

Similar results were noted on -6 to +16 mesh MgCl_2 of known heat treatment and the same material when crushed to -16 to +200 mesh size (Figure 33). For the latter, particle breakage to a powder occurred even when the steam flow rate was cut in half (liquid flow of 3 ml/hr). Initial rates for the above reactions were greater than their counterparts in which little powder was formed. The reason for the difference between different size particles of known heat treatment

Figure 32. $\text{MgCl}_2 \rightarrow \text{MgO}$ hydrolysis using MgCl_2 with different heat treatment histories

Figure 33. $\text{MgCl}_2 \rightarrow \text{MgO}$ hydrolysis using MgCl_2 with different heat treatment histories and/or particle sizes

is perplexing and the possibility of other factors interfering was examined. The reactor was cleaned under similar conditions for all runs and the quartz tubing in the reaction zone did become discolored after several runs. The quartz cloth and tubing placed on top of the bed maintained the bed position, but did not compress the bed as shrinkage occurred. It may be possible that the particular particle size distribution for -16 to +200 mesh size of known heat treatment self-supported itself in the bed preventing added strain from the high steam flow rate or maybe these particles have strength characteristics superior to other materials tested as a result of the recrystallization and screening process.

Chlorination of MgO to MgCl_2 was examined although efforts were curtailed due to emphasis on the hydrolysis reaction. The supply of -16 to +200 mesh MgCl_2 of known heat treatment was rapidly used and the remaining anhydrous MgCl_2 was found unsuitable for reasons previously discussed.

One chlorination run was made at 570°C on MgO prepared by hydrolysis of MgCl_2 at 570°C . Excess chlorine was run through the bed for one hour with some evolution of oxygen. Analysis of the base of the reactant bed indicated a surprising conversion of 85%. Of particular interest was the bed structure which had the characteristics of a porous solid as shown in Figure 34. It may be possible that problems associated with the contraction and expansion of the bed in going from the chloride to the oxide and vice-versa may be eliminated by alternating between a hypothetical 30 and 70% MgCl_2 composition in the porous solid. The

Figure 34. Porous solid product of $\text{MgO} \rightarrow \text{MgCl}_2$ chlorination

preceding would be strictly speculation as the chlorination was not reproduced and could have been accidentally catalyzed.

MgCl_2 - MgOHCl Cycle

Hydrolysis of MgCl_2 to MgOHCl was examined on -16 to +200 mesh MgCl_2 which had not been recrystallized. These particles did not break down during hydrolysis to MgOHCl nor did any appreciable change in bed volume occur. This may be related to no change in crystal structure. The rate of hydrolysis at 293°C shown in Figure 35 was easily reproduced and 100% conversion was approached during both runs from HCl evolution.

As little data was available on the kinetic stability of MgOHCl , a thermal decomposition run was made allowing a small flow of argon through the bed and raising the temperature 50°C every 15 min. The temperature at which HCl was monitored in the argon stream would then be the upper temperature limit for kinetic stability of MgOHCl and all chlorination runs would be required to be made at a lower temperature. This temperature was determined to be in the range of 485°C .

Chlorination of MgOHCl was performed once at about 470°C and a chlorine flow rate of 12 cc/min with a final bed composition of approximately 96% MgCl_2 . The amount of oxygen displaced volumetrically indicated conversion of only 25% with a leak in the system the probable source of error. Some water was evolved at the start of the reaction, possibly remaining from the hydrolysis reaction and could easily have been waters of hydration. The possibility of the Reverse Deacon reaction being catalyzed by the bed was not evident although not disproven.

Figure 35. $\text{MgCl}_2 \rightarrow \text{MgOHCl}$ hydrolysis at $\approx 292^\circ\text{C}$

DISCUSSION

The complexity of heterogeneous reactions and the variables associated with them became more evident as the experimental data was examined. Various attempts have been made by individuals to model heterogeneous reactions ranging from the rather simple approaches developed by Levenspiel (28, pp. 349-400) to increasingly sophisticated models requiring numerical solutions in solving the differential equations used for modeling. Szekely and associates (40-45) have developed a pore model and a grain model for nonflaking, isothermal particles with no structural change during reaction to model gas-solid reactions with a moving boundary. Both models define the reaction zone as occurring over a diffuse region as opposed to Levenspiel's shrinking core model assuming the reaction front to be distinct.

The data presented by da Cunha (11) for hydrolysis of MgCl_2 to MgO showed product conversion to be of an exponential nature with no data concerning steam flow rate given. It should be noted that the MgCl_2 sample, a product of titanium reduction, was melted and poured into molds before being crushed and screened.

The exponential nature of conversion is of direct contrast to that obtained in our experimental work where the rate was nearly linear over a large mole fraction range. The very small change in rates, a factor of 1.16 for a 125°C change in temperature for the -16 to +200 mesh material of known heat treatment plus the rapid increase in rate upon bed degradation and the formation of a fine powder would indicate diffusion to be the controlling factor. However the linear nature of

MgCl_2 conversion is of interest as it would not be expected for diffusion control. The resistance should increase and the reaction front area decrease at higher conversions reducing the overall rate assuming a shrinking core model applicable.

The grain model developed by Szekely and associates assumes diffusion to occur around grains of material with each grain then incorporating the shrinking core model. The pore model parallels Levenspiel's approach to gas reactions catalyzed by a porous solid. In this approach, there can be two principal diffusion terms. The first term is diffusion in the pore whereas the second is diffusion into the reacting bed. However both models reduce to the shrinking core model as diffusion resistance becomes controlling.

A rather unique observation may be made by comparing the hydrolysis runs to MgOHCl with those to MgO . Although the rate is slower and the temperature considerably less for hydrolysis to MgOHCl , the rate does not show the degree of linearity over the mole fraction range and more closely resembles data which could be associated to diffusion resistance in a shrinking core model. A change in crystal structure in going from MgCl_2 to MgO (hexagonal to cubic) plus the likelihood of the MgOHCl crystal to be hexagonal may be helpful in explaining the results. Very little if any particle degradation or bed shrinkage was noted for the MgCl_2 - MgOHCl hydrolysis or chlorination reactions whereas both were noted for the MgCl_2 - MgO hydrolysis. The linear or near linear rate could then have resulted from a diffusion controlled reaction coupled with some flaking of the MgO product resulting in decreased resistance and higher rates.

In earlier chlorination work on MgO performed at Ames Laboratory, a maximum conversion of 9.5% was obtained on MgO prepared by drying $\text{Mg}(\text{OH})_2$ (25). Since the reactivity has been found to be a function of heat treatment (9) and the previous heat treatment of the $\text{Mg}(\text{OH})_2$ was unknown, it was felt that MgO obtained through hydrolysis of MgCl_2 could have superior reactivity. The decision to use -16 to +200 mesh particles was to avoid fluidization problems and approach conditions ideal for a fixed bed reactor (Figure 6). It was hoped that the particles would not fall apart but rather maintain their structure although a 3.7 fold increase in size had been noted for the chlorination of MgO using carbon monoxide as a reducing agent (13). The experimental results confirmed the change in bed size as a 25% reduction in volume was noted for the hydrolysis reaction. Some particle degradation did occur during the hydrolysis reaction but in the one chlorination run that was made, an 85% conversion was obtained and formation of a porous solid noted, most likely a result of the MgO expansion upon chlorination. Although the chlorination run was performed only once for reasons previously cited, the potential for a MgCl_2 -MgO cycle based on formation of this porous solid does exist. To prevent the solid from falling apart, alternating between various bed compositions may be desirable as opposed to complete conversions. This approach should give a better overall rate as some diffusion resistance would be avoided.

Since the MgO particles formed may have a tendency to break down into a fine powder, particularly after the proposed cycle has been run in the alternating pattern a number of times, it may be more practical to abandon the fixed bed approach and to concentrate on fluidized beds

of MgCl_2 or MgO powder trying to increase rates by decreasing diffusion resistance and other problems associated with changes in particle size and crystal structure. A review of the very rapid rates obtained upon particle breakdown credits this approach as the powder could be transferred between the two reactors, one for hydrolysis and one for chlorination, by a pneumatic system. Such factors as energy required for fluidization and operation of the pneumatic system would be of major importance as would the rates.

The MgCl_2 - MgOHCl cycle in many respects could parallel the MgCl_2 - MgO cycle in development. Two major advantages are to be noted from this cycle. First, it is a low temperature cycle capable of utilizing heat from another reaction and second, problems associated with changes in bed volume appear to be minimal. The uncertainty in kinetic stability of MgOHCl plus twice the material being required for the same HCl evolution as for the MgCl_2 - MgO cycle at 100% conversion are major disadvantages. Both steps of the cycle are kinetically feasible and the effect of fluidization merits examination for reasons similar to the MgCl_2 - MgO cycle.

A very definite advantage of either cycle would be the exiting $\text{HCl-H}_2\text{O}$ concentration from the hydrolysis reaction as it relates to the work of separation. If rates of hydrolysis are sufficient, an $\text{HCl-H}_2\text{O}$ mixture may be fed into the hydrolysis reactor with an exiting concentration near equilibrium (86.5 mole percent HCl at 695°C for the MgCl_2 - MgO cycle). The $\text{HCl-H}_2\text{O}$ feedstream would be a combination of the azeotropic stream from the distillation column plus any make-up water required or one-half the HCl mole product. The azeotropic composition at 1 atm is

11.10 mole percent HCl (30). This approach would eliminate the HCl-H₂O separation below the azeotrope and allow a relatively easy separation of the HCl-H₂O mixture above the azeotrope (Figure 36).

Figure 36. Layout of fluidized bed reactor system

RECOMMENDATION

In the opinion of the author, research on the two cycles should be continued focusing in two distinct directions. First, the fixed bed reactions should be carefully examined due to the low work requirements to run the reaction and simplicity in design and initial capital investment. Second, increased energy requirements and a more complicated system may be justified in a fluidized bed reactor scheme if the rates of the $\text{MgCl}_2\text{-MgO}$ or $\text{MgCl}_2\text{-MgOHCl}$ reactions are greatly increased and equilibrium may be closely approached resulting in less total work of separation.

It is felt that the suggested reaction schemes may possess the potential of not only being suitable alternatives to the Reverse Deacon reaction, but may be superior approaches to obtaining the same end products when all factors are considered, particularly energy requirements for separation processes.

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APPENDIX. CLOSED THERMOCHEMICAL AND THERMOELECTROCHEMICAL CYCLES

Halide Processes

1. Calcium bromide process, De Beni, Euratom, 1970

	<u>Temperature, °K</u>
$\text{CaBr}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + 2\text{HBr}$	1000
$\text{Hg} + 2\text{HBr} + \text{HgBr}_2 + \text{H}_2$	520
$\text{HgBr}_2 + \text{Ca(OH)}_2 \rightarrow \text{CaBr}_2 + \text{HgO} + \text{H}_2\text{O}$	470
$\text{HgO} \rightarrow \text{Hg} + 1/2 \text{O}_2$	870

2. Strontium Bromide process, De Beni, Euratom, 1970

	<u>Temperature, °K</u>
$\text{SrBr}_2 + \text{H}_2\text{O} \rightarrow \text{SrO} + 2\text{HBr}$	1070
$2\text{HBr} + \text{Hg} \rightarrow \text{HgBr}_2 + \text{H}_2$	470
$\text{SrO} + \text{HgBr}_2 \rightarrow \text{SrBr}_2 + \text{Hg} + 1/2 \text{O}_2$	770

3. Manganese chloride process, De Beni, Euratom, 1972

	<u>Temperature, °K</u>
$6\text{MnCl}_2 + 8\text{H}_2\text{O} \rightarrow 2\text{Mn}_2\text{O}_4 + 12\text{HCl} + 2\text{H}_2$	970
$3\text{Mn}_3\text{O}_4 + 12\text{HCl} \rightarrow 6\text{MnCl}_2 + 3\text{MnO}_2 + 6\text{H}_2\text{O}$	370
$3\text{MnO}_2 \rightarrow \text{Mn}_3\text{O}_4 + \text{O}_2$	1170

4. Iron chloride process, Hardy, Euratom, 1972

	<u>Temperature, °K</u>
$6\text{FeCl}_2 + 8\text{H}_2\text{O} \rightarrow 2\text{Fe}_3\text{O}_4 + 12\text{HCl} + 2\text{H}_2$	920
$2\text{Fe}_3\text{O}_4 + 3\text{Cl}_2 + 12\text{HCl} \rightarrow 6\text{FeCl}_3 + 6\text{H}_2\text{O} + \text{O}_2$	450
$6\text{FeCl}_3 \rightarrow 6\text{FeCl}_2 + 3\text{Cl}_2$	690

Processes Based on the Reverse Deacon Reactions

1. Vanadium chloride process, Funk and Reinstrom, Allison Div., G.M., 1964

	<u>Temperature, °K</u>
$\text{H}_2\text{O} + \text{Cl}_2 \rightarrow 2\text{HCl} + 1/2 \text{O}_2$	970
$2\text{VCl}_2 + 2\text{HCl} \rightarrow 2\text{VCl}_3 + \text{H}_2$	300
$4\text{VCl}_3 \rightarrow 2\text{VCl}_4 + 2\text{VCl}_2$	970
$2\text{VCl}_4 \rightarrow 2\text{VCl}_3 + \text{Cl}_2$	300

2. Iron chloride process, De Beni, Euratom, 1972

	<u>Temperature, °K</u>
$\text{H}_2\text{O} + \text{Cl}_2 \rightarrow 2\text{HCl} + 1/2 \text{O}_2$	970
$2\text{HCl} + 2\text{FeCl}_2 \rightarrow 2\text{FeCl}_3 + \text{H}_2$	870
$2\text{FeCl}_3 \rightarrow \text{FeCl}_2 + \text{Cl}_2$	620

3. Iron chloride-iron oxide process, Hardy, Euratom, 1972

	<u>Temperature, °K</u>
$3\text{H}_2\text{O} + 3\text{Cl}_2 \rightarrow 6\text{HCl} + 3/2 \text{O}_2$	970
$3\text{Fe}_2\text{O}_3 + 18\text{HCl} \rightarrow 6\text{FeCl}_3 + 9\text{H}_2\text{O}$	390
$6\text{FeCl}_3 \rightarrow 6\text{FeCl}_2 + 3\text{Cl}_2$	690
$6\text{FeCl}_2 + 8\text{H}_2\text{O} \rightarrow 2\text{Fe}_3\text{O}_4 + 12\text{HCl} + 2\text{H}_2$	920
$2\text{Fe}_3\text{O}_4 + 1/2 \text{O}_2 \rightarrow 3\text{Fe}_2\text{O}_3$	620

4. Copper chloride process

	<u>Temperature, °K</u>
$\text{H}_2\text{O} + \text{Cl}_2 \rightarrow 2\text{HCl} + 1/2 \text{O}_2$	970
$2\text{HCl} + 2\text{CuCl} \rightarrow 2\text{CuCl}_2 + \text{H}_2$	470
$2\text{CuCl}_2 \rightarrow 2\text{CuCl} + \text{Cl}_2$	870

5. Chromium chloride process, Knoche, Julich, 1972

	<u>Temperature, °K</u>
$\text{H}_2\text{O} + \text{Cl}_2 \rightarrow 2\text{HCl} + 1/2 \text{O}_2$	970
$2\text{HCl} + 2\text{CrCl}_2 \rightarrow 2\text{CrCl}_3 + \text{H}_2$	470
$2\text{CrCl}_3 \rightarrow 2\text{CrCl}_2 + \text{Cl}_2$	1070

6. HCl thermal decomposition process

	<u>Temperature, °K</u>
$\text{H}_2\text{O} + \text{Cl}_2 \rightarrow 2\text{HCl} + 1/2 \text{O}_2$	970
$2\text{HCl} \rightarrow \text{H}_2 + \text{Cl}_2$	1070

Iron Oxide and Carbon Oxide Processes

1. Steam-iron-CO₂ process, Von Fredersdorff, IGT, 1959

	<u>Temperature, °K</u>
$\text{Fe} + \text{H}_2\text{O} \rightarrow \text{FeO} + \text{H}_2$	820 to 1220
$3\text{FeO} + \text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2$	
$\text{Fe}_3\text{O}_4 + \text{CO} \rightarrow 3\text{FeO} + \text{CO}_2$	
$\text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2$	
$2\text{CO}_2 \rightarrow 2\text{CO} + \text{O}_2$	590

2. Carbon-steam-iron process, Marchetti-De Beni, Euratom, 1970

	<u>Temperature, °K</u>
$\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$	920
$\text{CO} + 2\text{Fe}_3\text{O}_4 \rightarrow \text{C} + 3\text{Fe}_2\text{O}_3$	520
$3\text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe}_3\text{O}_4 + 1/2 \text{O}_2$	1670

Metal and Alkali Metal Processes

1. Tin oxide process, Souriau, Gaz De France, 1972

	<u>Temperature, °K</u>
$\text{Sn} + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{SnO}_2$	670
$2\text{SnO}_2 \rightarrow 2\text{SnO} + \text{O}_2$	1970
$2\text{SnO} \rightarrow 2\text{NO}_2 + \text{Sn}$	970

2. Manganese-sodium oxide process, De Beni, Euratom, 1972

	<u>Temperature, °K</u>
$\text{Mn}_2\text{O}_3 + 4\text{NaOH} \rightarrow 2\text{NaO} \cdot \text{MnO}_2 + \text{H}_2\text{O} + \text{H}_2$	1070
$2\text{NaO} \cdot \text{MnO}_2 + \text{H}_2\text{O} \rightarrow 2\text{NaOH(aq)} + 2\text{MnO}_2$	370
$2\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 + 1/2 \text{O}_2$	870

Thermoelectrochemical Processes (32, p. 90)

1. Hydrogen chloride electrolytic process

	<u>Temperature, °K</u>
$\text{H}_2\text{O} + \text{Cl}_2 \rightarrow 2\text{HCl} + \frac{1}{2} \text{O}_2$	973
$2\text{HCl} \rightarrow \text{H}_2 + \text{Cl}_2$	(Electrolysis)

2. Mercury chloride process

	<u>Temperature, °K</u>
$\text{H}_2\text{O} + \text{Cl}_2 \rightarrow 2\text{HCl} + \frac{1}{2} \text{O}_2$	973
$2\text{Hg} + 2\text{HCl} \rightarrow 2\text{HgCl} + \text{H}_2$	573
$2\text{HgCl} \rightarrow 2\text{Hg} + \text{Cl}_2$	(Electrolysis)

3. Iron chloride electrolysis process

	<u>Temperature, °K</u>
$\text{H}_2\text{O} + \text{Cl}_2 \rightarrow 2\text{HCl} + \frac{1}{2} \text{O}_2$	973

(Electrolysis)

448

423

4. Copper chloride electrolytic process

Temperature, °K

973

(Electrolysis)

573