

THERMOGRAVIMETRIC ANALYSIS OF CARBO-CHLORINATION OF A CLAY

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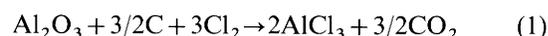
A thermogravimetric analysis has been made on the carbo-chlorination of a clay. The chlorination at lower reaction temperatures showed an increase in weight over an initial short period, while the chlorination at higher temperatures did not. The chlorination rate increases with time initially, reaches a maximum and decreases rapidly thereafter. The mechanism of the rapid decrease of reaction rate was investigated with regard to various aspects.

Introduction

Aluminum chloride (AlCl_3) is a colorless, crystalline, very moisture-sensitive substance that finds wide application in organic chemistry. Aluminum chloride is also a potential source for the production of aluminum metal. It has been produced commercially by reacting aluminum metal with chlorine. However, alumina, bauxite or clay could be more economical sources for the production of aluminum chloride. There are many patents on the chlorination of

alumina, bauxite and clay to produce aluminum chloride, but there are only a few published reports on the reaction kinetics. To our best knowledge the first literature reference appeared in 1975^{1,2)}. Several papers have been published since then^{3-5,8)}. The present work is to study the reaction kinetics of chlorination of a clay, the chemical composition of which is shown in **Table 1**, using a thermogravimetric analyzer.

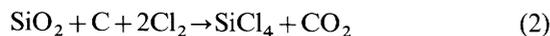
Major reactions occurring during the chlorination of clay in the presence of carbon are represented by



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Table 1. Chemical composition of clay, wt%

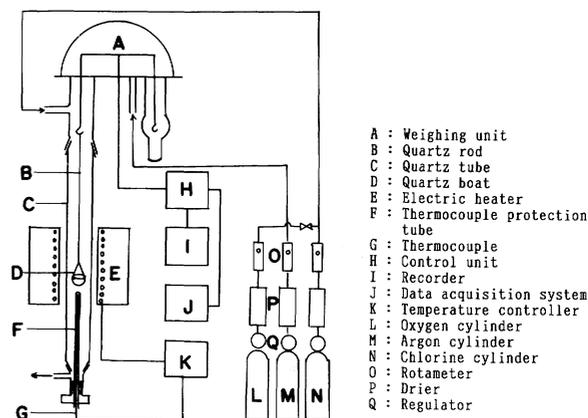
Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	MnO	CaO	MgO	Na ₂ O	TiO ₂	P ₂ O ₅	K ₂ O	H ₂ O
37.86	44.03	1.46	0.02	0.85	0.78	0.33	0.20	0.09	1.53	11.8



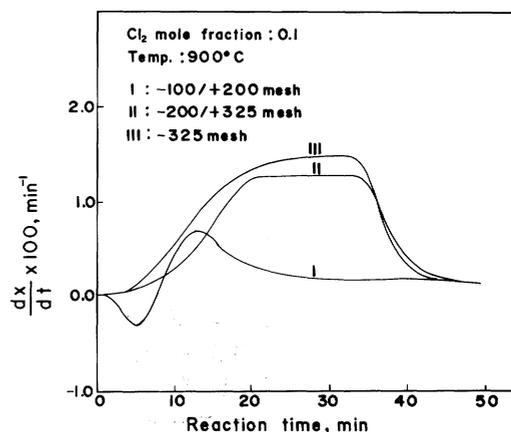
In the chlorination of the clay, not only reactions (1) and (2) but also other chlorination reactions for the metals present as impurities in the clay occur simultaneously. The thermogravimetric analyzer gives the net change in weight caused by all the reactions, but provides no individual reaction rates. However, the chlorination reaction rate for aluminum is much higher than for silicon and the weight fraction of those impurities in the clay is low as shown in Table 1. Therefore, thermogravimetric analysis would provide some valuable information on the chlorination of aluminum with a careful analysis of the weight-change measurement data.

1. Experimental

The chlorination rates were measured by a micro-balance (CAHN-1000). **Figure 1** shows the experimental apparatus. The sample is placed in a quartz boat (8 mm in diameter and 6 mm in depth) suspended by a 1-mm quartz rod from the balance. The reactor is made of quartz (2 cm in diameter and 50 cm in length) and is vertically mounted with a surrounding electrical heater. The reaction temperature is measured by a thermocouple in a thin 6 mm-diameter quartz tube projecting upward from the bottom of the reactor to within two millimeters of the sample. The weight of clay remaining after the reaction is measured by burning off the carbon in the mixture. The clay is calcined at 700 °C for one hour, then mixed with activated carbon (CALCON, type CAL 12 × 40) at a predetermined ratio. The reason for calcining the clay is to drive out chemically bound water so that reactive sites can be created. The weight of sample of clay-carbon mixture in one batch is 60–80 mg. Argon is used as purge and carrier gas. Argon and chlorine are passed through separate driers packed with molecular sieve to remove water. The flow rate of argon-chlorine mixture is maintained at 100 ml/min. In a preliminary test the flow rate was increased up to 300 ml/min, but no significant change in the reaction rate was observed. The activated carbon is treated with acids to remove impurities to less than 0.5%. The activated carbon has a surface area of 1,000 m²/g. The particle sizes of both the clay and the activated carbon are under 325 mesh. The average particle size of the clay is 17 μm and the cumulative volume of the pores up to 10 μm is 0.25 cm³/g.

**Fig. 1.** Schematic drawing of the experimental apparatus**Table 2.** Operating conditions for chlorination

Pressure	: atmospheric
Temperature, °C	: 900
Chlorine mole fraction	: 0.1
Clay/activated carbon ratio	: 1.0
Particle sizes of clay and carbon	: under 325 mesh
Sample weight, mg	: 60–80
Purge gas rate, ml/min	: 100

**Fig. 2.** Effect of particle size on reaction rate

2. Results and Discussion

All the experimental results to be discussed were obtained at the operating conditions listed in **Table 2** unless stated otherwise. dx/dt shown in the abscissas of **Fig. 2** through **Fig. 6** indicates the rate of dimensionless weight change, defined as follows:

$$\frac{dx}{dt} = \frac{-1}{W_0} \frac{dW}{dt} \quad (3)$$

where W_0 is the initial weight of clay and W is the instantaneous weight. dx/dt represents the overall reaction rate.

Figure 2 shows the effect of particle size on the chlorination rate. The chlorination rate increases with decreasing particle size, implying that the resistance through the pores plays an important role in determining the reaction rate. To find the particle size at which the reaction is chemically controlled, classification under 325 mesh may be necessary, but such a fine classification was not attempted in the present study. The sample weight was varied from 60 mg down to 8 mg, but no significant change in the reaction rate was observed, implying that the resistance to interparticle diffusion is negligible.

Figure 3 shows the reaction rates at three temperatures with the chlorine mole fraction fixed at 0.1. At 700°C the sample gains weight initially; the gain was 4.3 wt% of the original sample weight. At 800°C the initial gain is also observed, but is not so high as at 700°C. However, at 900°C no initial gain is observed. In a carbo-chlorination of kaolin catalyzed by NaCl, such initial gain was reported; this phenomenon was claimed to be due to the formation of less volatile NaAlCl_4 ³⁾. In the present experiment, NaCl is not used. However, the alkali and alkali earth oxides present in the clay (CaO , 1.85 wt%; MgO , 0.78 wt%; Na_2O , 0.33 wt%; K_2O , 1.53 wt%) may be reacted with chlorine to form molten chlorides which remain in the clay, thereby contributing to the gain. The chlorination of these metals is known to take place preferentially over that of aluminum⁶⁾. The gain is also partially due to the adsorption of chlorine on activated carbon having such a high surface area as 1000 m²/g; about 2.0 wt% of gain was observed at 700°C due to the adsorption. As the temperature is increased, the gain was observed to decrease, probably because the rate of aluminum chlorination acting to reduce the weight of clay increases exponentially.

Figure 4 shows that the reaction rate drops rapidly in 20 to 30 minutes, causing the reaction to cease while the conversion is 20 to 25% only. Since the chlorination rate of aluminum oxide is higher than that of silicon oxide²⁾, the weight ratio of Si to Al in the clay increased after the reaction from 1.11 to 1.21. However, the ratio of 1.21 after the reaction indicates that a considerable amount of aluminum remains unreacted after the reaction decayed. SiCl_4 formed by chlorination of the silicon dioxide in the clay is known to retard the chlorination rate⁷⁾. To measure this retardation effect, three different samples were chlorinated at the same reaction condition: clay from which aluminum is removed by hydrochloric acid (SiO_2 , 91.6 wt%; Al_2O_3 , 5.0 wt%), α -alumina, and a mixture of the two in equal pro-

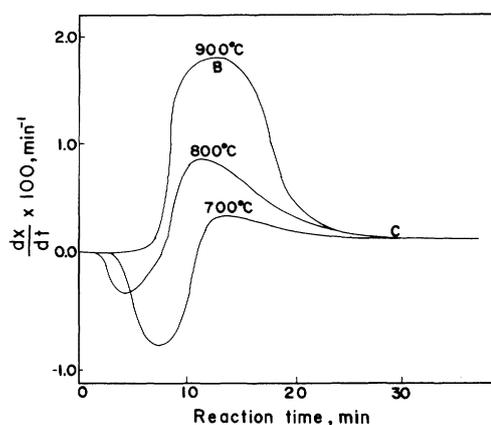


Fig. 3. Effect of reaction temperature on reaction rate

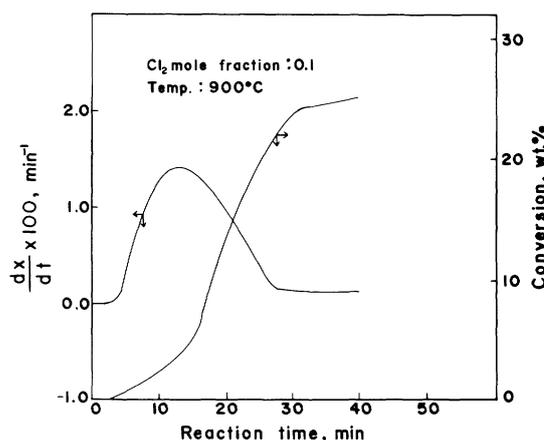


Fig. 4. Change of reaction rate and conversion with time

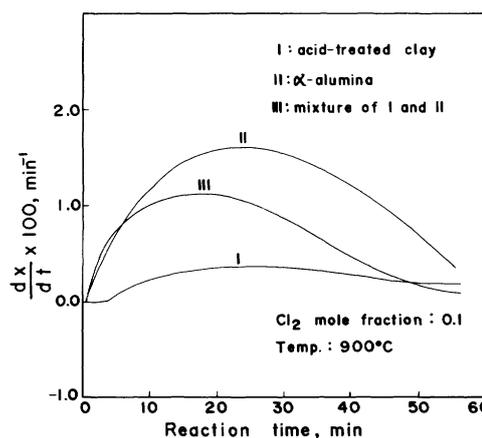


Fig. 5. Reaction rates for acid-treated clay, α -alumina and mixture of α -alumina and acid-treated clay

portions (this mixture is expected to have reaction characteristics similar to those of the clay). The reaction rates measured are shown in Fig. 5. The reaction rate is highest with the α -alumina and lowest with the acid-treated clay, the reaction rate of the mixture lying between the two. The reaction rate for the mixture does not show such a rapid decrease as observed in the chlorination of the clay. This implies

that retardation by SiCl_4 was not a major cause of the rapid decrease of reaction of the clay.

The reaction rate would be proportional to the surface area of a solid reactant if the other reaction variables are kept constant. The surface area of the clay at which the reaction rate is maximum (point "B" in Fig. 3) was $21.7 \text{ m}^2/\text{g}$ and at point "C" where the reaction has almost ceased, it was $10.8 \text{ m}^2/\text{g}$. This means that such a rapid drop in reaction rate cannot be explained by the change of reaction surface area.

X-ray diffraction analyses of the clay before reaction and after reaction showed no detectable transformation during the reaction, indicating that the rapid drop of reaction rate was brought about by mechanisms other than phase transformation.

Table 3 shows the weight ratios of Si to Al measured at three reaction times using three different analyzers: an X-ray photo-electron spectroscope (XPS), a proton induced X-ray emission (PIXE) analyzer and a inductively coupled plasma (ICP) analyzer. The distance inward from the surface of a particle which each analyzer can cover or the depth resolution varies with type of analyzer. It is 100 \AA for the XPS and $5 \mu\text{m}$ for the PIXE. The ICP gives the average composition of the whole particle. In the chemical reaction control regime the three analyzers would give the same result because the reaction proceeds uniformly throughout the particle, while in the pore-diffusion control regime the ratio of Si to Al, which indicates the extent of reaction, must be locally different for a clay particle. Therefore, the three analyzers, having different depth resolutions, would give different results. Table 3 indicates that the ratio of Si to Al increases with reaction time and decreases with increasing distance from the surface, implying that the chlorination reaction is faster for aluminum than for silicon and that the overall reaction is in the pore-diffusion control regime. This means that there exists a considerable resistance for chlorine to diffuse into the clay particle.

The alkali and alkali earth metal chlorides formed during the reaction may provide a significant resistance to the diffusion of chlorine since the chlorides are liquid at 900°C . It may be assumed that the reaction is controlled initially by chemical reaction (this may be verified by calculating the Thiele modulus), then moves to the pore-diffusion control regime as those liquid chlorides are formed and diffuse to plug the pores. The Thiele modulus at the initial condition is calculated using equation (4), assuming the reaction order is $1.0^{(8)}$.

$$\Phi = R_p(k_v/D_e)^{0.5} \quad (4)$$

where R_p is the radius of a clay particle, k_v is the rate constant, and D_e is the effective diffusivity. The

Table 3. Chemical analysis of the clay at different reaction times

Reaction time, min	0	20	60
Weight ratio of Si to Al			
XPS	1.41 (1.00)	4.10 (2.91)	4.63 (3.28)
PIXE	1.34 (1.00)	1.55 (1.16)	1.94 (1.45)
ICP	1.11 (1.00)	1.18 (1.06)	1.21 (1.09)

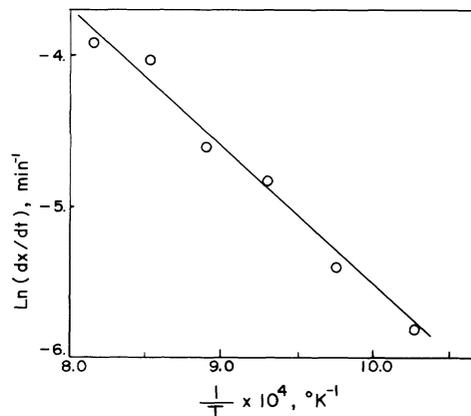


Fig. 6. Reaction rate vs. reciprocal of temperature

porosity of the clay in terms of void fraction is 0.56 and the average particle size is $17 \mu\text{m}$. The effective diffusivity of chlorine is calculated to be $0.387 \text{ cm}^2/\text{sec}$ assuming that the effective diffusivity is proportional to the square of porosity. The activation energy and the preexponential factor are estimated to be 75.3 KJ/g mole and $5.33 \times 10^5 \text{ cm}^3/\text{g mole}/\text{sec}$ respectively from **Fig. 6**. The maximum rate for each temperature was used for the Arrhenius plot in **Fig. 6**; this may be good enough for a rough estimation of the control regime. Using the above data, the Thiele modulus at 900°C was calculated as 3.9×10^{-3} , which indicates that the reaction is definitely in the chemical reaction control regime; at a Thiele modulus of less than 1.0, the reaction is chemically controlled⁽¹⁰⁾.

Based on the observed reaction rate constants and the physical properties, the chlorination of clay was expected to be chemically controlled, but was actually controlled by diffusion. The formation of the liquid chlorides appears to be closely related to the reaction being diffusion-controlled and consequently with the rapid decrease in reaction rate.

Conclusion

The reaction showed an initial gain in weight due to the formation of alkali and alkali earth chlorides and to the absorption of reactant gas on the activated carbon. Based on the experimental results that the reaction rate is affected by the size of particles and that the extent of reaction decreases with distance from the surface, it could be concluded that the

reaction is in the pore-diffusion control regime. Initially the reaction may be in the chemical control regime, but is changed to a pore-diffusion controlled reaction due to the formation of alkali and alkali earth chlorides which are in liquid state at the reaction temperature. The cessation of reaction in 20 to 30 minutes appears to be caused by the formation of molten alkali and alkali earth chlorides which would resist the diffusion of chlorine.

Nomenclature

D_e	= effective diffusivity	[cm ² /sec]
k_v	= rate constant	[1/sec]
R_p	= radius of a clay particle	[cm]
t	= time	[sec]
W	= instantaneous weight	[g]
W_0	= initial weight	[g]
dx/dt	= overall reaction rate	[1/sec]

Φ = Thiele modulus

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