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NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

Hydrothermal dechlorination of PVC in the presence of ammonia

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Abstract Poly(vinyl chloride) (PVC) powder and commercial rigid PVC pipe were dechlorinated hydrothermally in the presence of alkalis such as ammonia, sodium hydroxide, and potassium hydroxide in a semi-batch flow reactor, with comparison to dechlorination using water alone. Aqueous ammonia was the most effective among these solvents. Dechlorination with aqueous ammonia proceeded in three stages: initial incubation, major dechlorination, and slow dechlorination. In the initial stage the rates were very slow and scarcely affected by temperature or ammonia concentration. In the second stage extensive dechlorination took place, and the rates were affected by temperature and ammonia concentration. These higher rates were found to be significantly influenced by swelling, not alkalinity, when these various alkalis solvents were compared. In the last stage the rates were slower than in the previous stage, and were not significantly dependent on temperature or ammonia concentration.

Introduction

Poly(vinyl chloride) (PVC)accounts for ca. 15% [1] of the total plastic production in Japan, and has been used widely in consumer and industrial products. Therefore, a very large amount of plastic waste containing PVC is discharged. In Japan most of this is disposed of in landfills and by incineration. Due to the increasing need for plastic waste recycling, a growing amount of chlorine-containing plastic waste has to be dechlorinated because toxic compounds could possibly be emitted in the course of their disposal. Many efforts have been made to remove chlorine from PVC or PVC-containing materials: pyrolysis in vacuum or an inert atmosphere [2–5], and dechlorination hydrothermally or under supercritical conditions [6–13], photochemically [14–16] or mechano-chemically [17, 18]. Among these treatments, hydrothermal dechlorination is attractive due to its relatively low operating temperature and almost complete recovery of the resulting chlorine in a liquid medium. Yoshioka and coworkers [7, 9–11] have studied the hydrothermal dechlorination of various PVCs and its products with sodium hydroxide in the presence/absence of oxygen. They found that the addition of sodium hydroxide increased the reaction rate. Thus, the addition of alkali was effective for the hydrothermal dechlorination of PVC. Here, ammonia is examined as an alternative to sodium hydroxide. Ammonia is formed in abundance as a side-product from treatment of nitrogenous wastes such as sewage sludge, food wastes, and wastewater from farm animal yards. The objective of this study was to demonstrate the effectiveness of using ammonia instead of other alkalis in the hydrothermal dechlorination of PVC.

Experimental

Dechlorination of PVC powder (Kanto Chemical Co., Tokyo, Japan), and that of a commercial rigid PVC pipe (chlorine content 44.6 wt.%) were carried out in a semi-batch flow reactor. A schematic diagram of the experimental apparatus is shown in Fig. 1. The reactor was made of stainless-steel tubing with an inner volume

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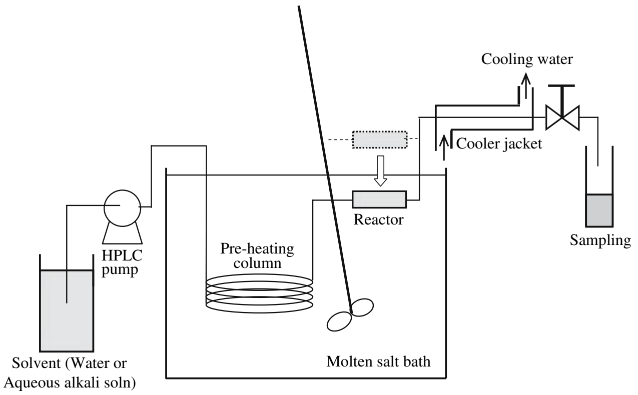

Fig. 1 A schematic diagram of the semi-batch flow reactor

of 3.5 mL. A PVC sample (50 mg) wrapped loosely with a stainless-steel screen was placed in the reactor at room temperature. The preheating column, made of 1/8 inch stainless steel tubing (2.17 mm I.D. × 3 m long), was placed in a molten salt bath, whose temperature was regulated within ±2 °C. The preheating column, the reactor and all lines were filled with distilled water. At time zero, the solvent (distilled water or aqueous alkali) was fed by an HPLC pump at a constant flow rate, generally 3 mL/min (ambient conditions), and the reactor was immersed in the molten salt bath. The pressure was maintained at 10 ± 0.1 MPa by a back pressure regulator operated by a high-frequency electromagnetic open-shut valve. The temperature of the reactor was measured with a thermocouple inserted in the reactor, and was found to reach the set value within 1 min under all conditions. The product solution that eluted from the back pressure regulator was collected at fixed intervals, usually 2 min. After a certain heating time had elapsed, the reactor was removed from the bath, cooled in cold water, and opened. The residual solid was recovered, and weighed after drying. The chlorine content of the initial samples and corresponding residual solids were measured by a combustion method: the residual solid was burned with oxygen in a 1 L glass flask, and the chlorine thereby generated was absorbed in aqueous NaOH. The chloride contents of the resulting solutions were determined by ion chromatography. The swelling of PVC powder was measured in a cell with a volume of ca. 11 mL, equipped with quartz windows, and heated from room temperature to 460 K at a rate of ca. 4.8 K/min using four heating rods mounted in the cell body. The degree of swelling was measured from photos taken by a digital camera every 30 s. The nitrogen and carbon content of the residual solids were measured by a CHNS/O analyzer (Model 2400, Series II, Perkin Elmer Japan, Tokyo).

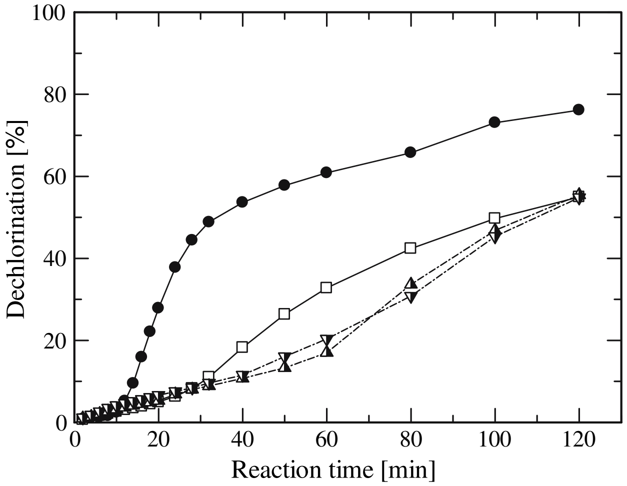

Fig. 2 Dechlorination as a function of time at 503 K using aqueous alkalis at a concentration of 0.06 M: ammonia (●), NaOH (▼), KOH (▲), and water (□)

Results and discussion

PVC powder

Figure 2 compares the effects of various alkalis on the dechlorination of PVC powder at 503 K. Aqueous ammonia was remarkably more effective in dechlorination than the strong bases NaOH and KOH, or water. In the initial stage up to 10 min, the degree of dechlorination was almost the same for all solvents, and increased linearly with time. After 10 min, the dechlorination rate for ammonia suddenly increased steeply until 30 min, and increased gradually thereafter. With NaOH and KOH, dechlorination increased approximately linearly with time up to 60 min, after which the rate increased. Dechlorination with water was also proportional to time until 30 min, after which the rate increased, and finally increased more gradually. Dechlorination with water was slightly higher than with NaOH or KOH from 30 to 100 min, but the results were comparable at 120 min.

Figure 3 shows scanning electron microscopic pictures of residual solids after dechlorination at 503 K for 120 min with (a) water, (b) 0.6 M NaOH, and (c) 0.6 M aqueous ammonia. Many pores were observed in the residual solid with 0.6 M ammonia but not on the surface. In contrast fewer pores were seen with water and aqueous NaOH. It was found that the residual solid was significantly more swollen in ammonia than in water or NaOH, as will be described later. Georgiev et al. [19] have pointed out that diffusion-controlled release of hydrogen chloride was critical to the thermal dehydrochlorination behavior of PVC, and Patel et al. [20] have mentioned that the

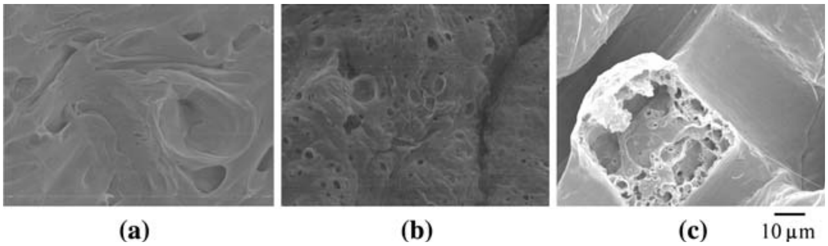

Fig. 3 Scanning electron microscopic photos of residual solids after dechlorination at 503 K for 2 h with (**a**) water, (**b**) 0.6 M NaOH, and (**c**) 0.6 M ammonia

dechlorination rates were dependent on particle size. It was also considered that amino groups could have been added to residual solid by nucleophilic substitution reactions, but the nitrogen content of the residual solids was lower than 2 wt.% after treatment with 0.6 M ammonia at 503 K for 2 h. Thus, either this reaction was unlikely, or amino groups substituted onto residual solid quickly decomposed under these hydrothermal conditions.

Figure 4 shows the residual chlorine content (expressed as the ratio to the initial chlorine content) of powder samples treated with 0.6 M ammonia at various temperatures from 483 to 523 K, as a function of time. As depicted, the dechlorination rates in the three stages could be represented by first order reaction kinetics with respect to residual chlorine content of the solid:

$$-\frac{\mathrm{d}C}{\mathrm{d}t} = k_i C \qquad (1)$$

where k_i is the rate constant for the i-th stage. Note that chlorine removed from the residual solid could be assumed to have been rapidly swept out of the reactor because the fluid residence time in the reactor was less than 15 s, as indicated by a tracer response measurement [21].

The dechlorination rate k_1 in the first stage was very slow and nearly independent of temperature. Vigorous dechlorination took place in the second stage, and the rate k_2 was strongly influenced by temperature. In the subsequent stage, the dechlorination rate k_3 was slow, and again nearly independent of temperature.

Figure 5 shows the residual chlorine content of powder samples treated at 503 K with various concentrations of ammonia ranging from zero (water) to 6 M, as a function of time. Similar to the dechlorination at various temperatures shown in Fig. 4, this dechlorination also proceeded in three stages. In the first stage the dechlorination rate seemed nearly independent of ammonia concentration. In the second stage the rate showed strong concentration dependence, represented by the steep straight lines in the plots. In the third stage, the rate was slow, and again was not significantly affected by ammonia concentration. In particular, at lower concentrations, the rates were nearly the same. It was postulated that the rate in the last stage was controlled by diffusion of chlorine in the solid sample.

Figure 6 shows Arrhenius plots for the rate constant k_2 (in the major, second, dechlorination stage) for powder and rigid PVC pipe treated with various solutions. The values of the activation energies and the pre-exponential factors are listed in Table 1. The rates increased in the order: water <1 M NaOH <0.6 M ammonia, with the ammonia

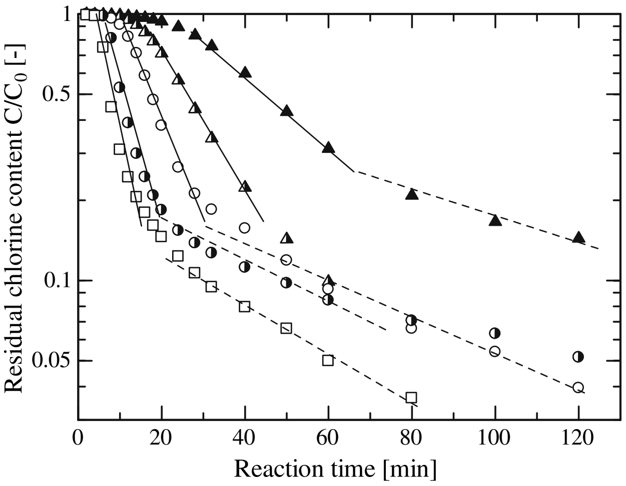

Fig. 4 Residual chlorine content of powder samples treated with 0.6 M ammonia at various temperatures, namely 483 K (▲), 493 K (◭), 503 K(○), 513 K (◑), and 523 K (□), as a function of time

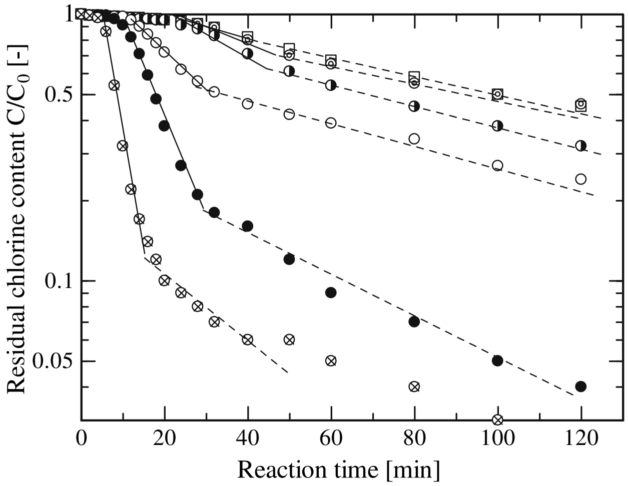

Fig. 5 Residual chlorine content of powder samples treated at 503 K with aqueous ammonia solutions of various concentrations: 0.0006 M (◎); 0.006 M (◑); 0.06 M (○); 0.6 M (●); 6 M (⊗); and water (□), as a function of time

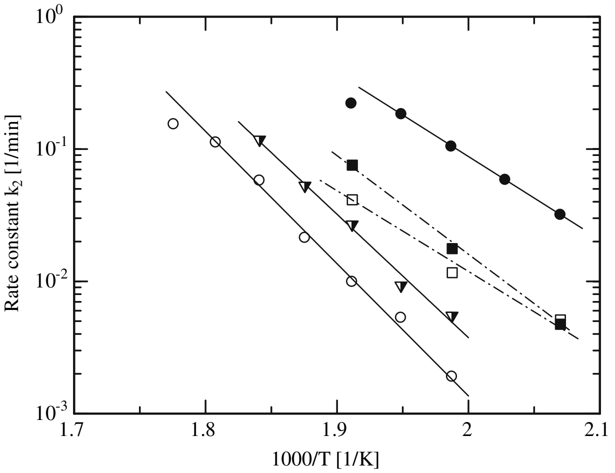

Fig. 6 Arrhenius plots for powder treated with various solutions: water (○), 1 M NaOH (▼), and 0.6 M ammonia (●), and for rigid PVC pipe treated with water (□) and 0.6 M ammonia (■)

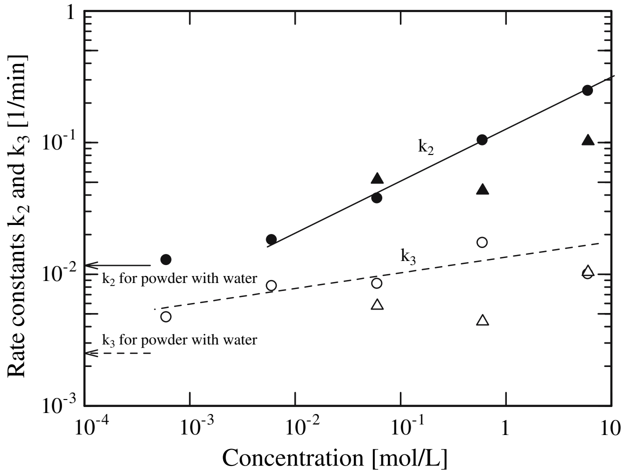

Fig. 7 Concentration dependence of rate constants k_2 for powder (●) and pipe (▲), and k_3 for powder (○) and pipe (△), treated with aqueous ammonia at 508 K

Table 1 Pre-exponential factors and activation energies of the first order reaction rate constants for dechlorination of PVC powder and rigid PVC pipe with various solvents in the major (second) dechlorination stage

Solvent	Pre-exponential factor (1/min)	Activation energy (kJ/mol)	Effective temperature range (K)
PVC powder			
Water	5.23×10^{16}	187	503–563
0.6 M aq. ammonia	3.03×10^{11}	120	483–523
1 M aq. NaOH	1.73×10^{16}	179	503–543
Rigid PVC pipe			
Water	3.17×10^{9}	109	483–523
0.6 M aq. ammonia	2.23×10^{13}	145	483–523

solution being remarkably effective. The rates for the pipe sample will be discussed later.

Figure 7 shows the effects of ammonia concentration on the rate constants k_2 and k_3 (in the final stage), for powders and rigid PVC pipe treated with aqueous ammonia and with water at 503 K. The rate constant k_2 for powder showed a strong dependence on ammonia concentration with a slope of 0.38 in this double-logarithmic plot, but k_3 was not significantly affected. When the ammonia concentration approached zero, k_2 and k_3 seemed to reach the asymptotic value for water. The effect for the pipe will be discussed in the later section.

Mixed solvents

Figure 8 depicts the dechlorination of powder samples treated with various mixed solutions and with water at 503 K, as a function of time. Dechlorination with 0.6 M ammonia was more effective than with 0.6 M $(NH_4)_2SO_4$, 0.06 M ammonia + 0.6 M NaOH, 0.06 M ammonia + 0.06 NaOH or 0.06 M ammonia. It was interesting to note that the dechlorination curve for 0.06 M ammonia was identical to those of 0.06 M ammonia in the presence of NaOH at different concentrations in the first and the second dechlorination stages. Dechlorination in the second stage was affected only by the ammonia concentration, irrespective of NaOH concentration, which ranged from 0 to 0.6 M. The rates in the third stage were slightly influenced by alkalinity at different NaOH concentrations.

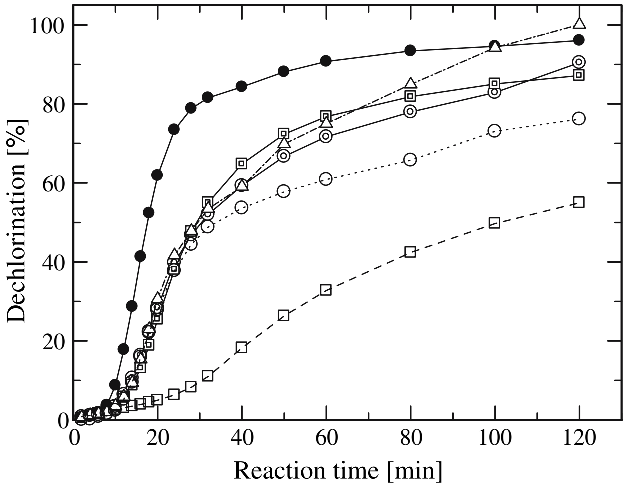

Fig. 8 Dechlorination of powder samples treated with various mixed solutions and with water at 503 K, as a function of time: 0.6 M ammonia (●), 0.6 M $(NH_4)_2SO_4$ (△), 0.06 M ammonia (○), 0.06 M ammonia + 0.06 M NaOH (◎), 0.06 M ammonia + 0.6 M NaOH (▣), and water (□)

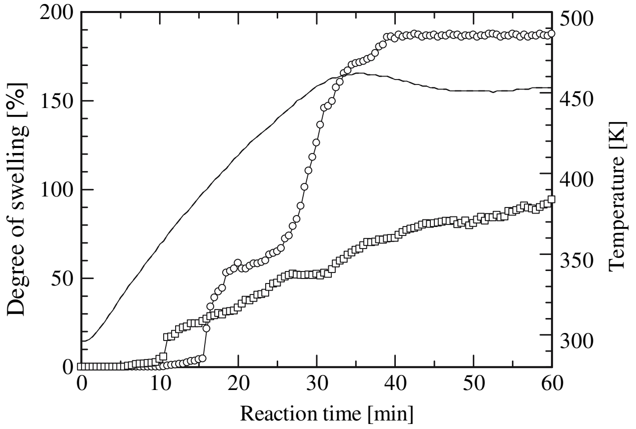

Fig. 9 Effect of ammonia on degree of swelling of powder as a function of temperature for treatment with 6 M ammonia (○) and water (□). Temperature is shown as a solid line (—) in this plot

Degree of swelling

Figure 9 plots the degree of swelling for powders treated with 6 M ammonia or water, heated from room temperature to 453 K at a rate of 4.8 K/min and subsequently held at that temperature for a period of time. The presence of ammonia significantly increased the degree of swelling, which was almost twice as high as that obtained with water. If the reaction was controlled by diffusion of released chlorine in the solid sample, the degree of swelling could have directly affected the rates. In fact, many pores were seen in SEM photos of the residual solids, as shown in Fig. 3(c).

Rigid PVC pipe

Figure 10 depicts the dechlorination of rigid PVC pipe with 0.6 M ammonia and pure water at three temperatures: 483, 503 and 523 K, as a function of time. In every case, ammonia was more effective than water. At each temperature, the incubation period, when the rates depended neither on temperature nor on alkali concentration, was much shorter than for pure water.

Figure 11 shows the effect of ammonia concentration on the dechlorination rate at 503 K. As seen for the powder, the dechlorination rate for rigid PVC increased with increasing ammonia concentration. For the powder, the effect at 0.6 M was more pronounced than at 0.06 M, but this difference was small for rigid PVC. This may have resulted from the difference in the effect of ammonia on the degree of swelling.

Arrhenius plots are shown in Fig. 6 for the rate constant k_2 for the second dechlorination stage of rigid PVC pipe with pure water and 0.6 M ammonia, compared to those obtained earlier for PVC powder. As seen for the powder, the effect of ammonia on the rates k_2 was significant for rigid PVC, but less so. In fact, the rate constants for pipe seemed to increase with increasing ammonia concentration, but with more scatter in the data shown in Fig. 7. The k_3 values were not evidently influenced by ammonia concentration.

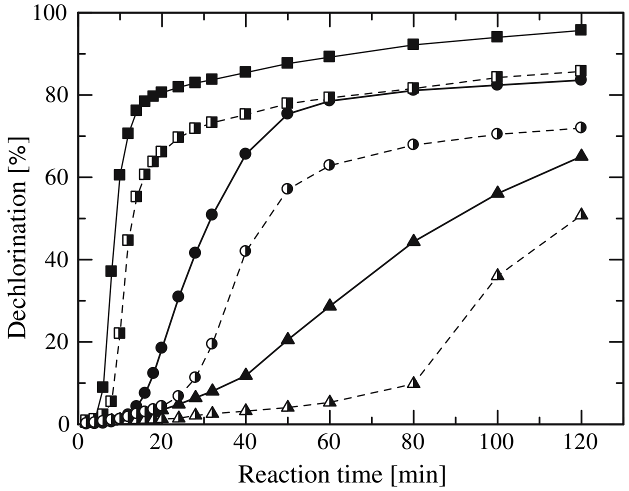

Fig. 10 Dechlorination of rigid PVC pipe with 0.6 M ammonia and pure water at three temperatures: 483, 503 and 523 K, as a function of time. Ammonia: 483 K (▲), 503 K (●) and 523 K (■); water: 483 K (◭), 502 K (◑) and 523 K (◨)

Conclusions

PVC powder and commercial rigid PVC pipe were dechlorinated at different temperatures with water at

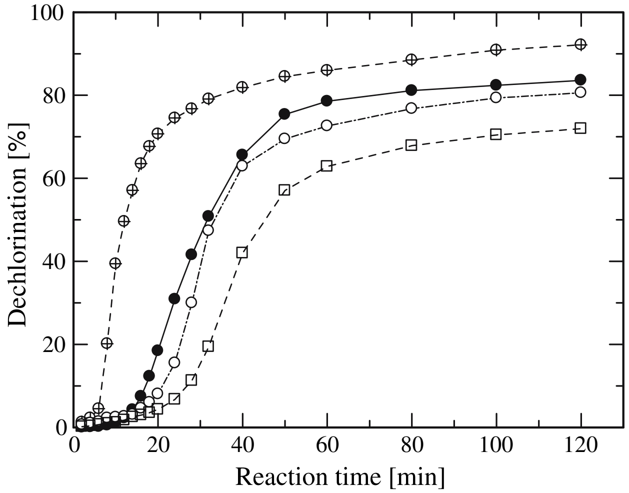

Fig. 11 Dechlorination of rigid PVC pipe at 503 K as a function of time, upon treatment with water (□), and various concentrations of ammonia: 0.06 M (○), 0.6 M (●) and 6 M (⊕)

10 MPa in the presence of various alkalis such as ammonia, sodium hydroxide, and potassium hydroxide. Aqueous ammonia was significantly more effective than the various other solvents studied, and the dechlorination rates increased with increasing ammonia concentration. The presence of ammonia resulted in significant swelling compared to other alkali solutions and water. The dechlorination reaction in aqueous ammonia could be classified into three stages: (1) In the initial incubation period, the rates were only slightly influenced by temperature and ammonia concentration. (2) In the major (second) dechlorination stage, the reaction proceeded vigorously and the rate was affected by temperature and ammonia concentration. (3) In the final stage, where the rate may have been controlled by diffusion of released chlorine in the residual solid, the rates were not significantly influenced by temperature or ammonia concentration. In the major stage of dechlorination in mixed aqueous solutions of 0.06 M ammonia with various concentrations of NaOH, the rates were not significantly influenced by NaOH concentration.

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