Extraction and Mutual Separation of Rare Earths from Used Polishes by Chemical Vapor Transport
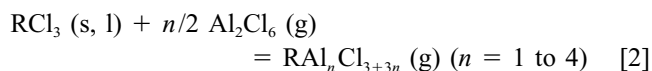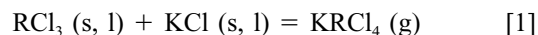
TETSUYA OZAKI, KEN-ICHI MACHIDA, and GIN-YA ADACHI

A dry recovery process for rare earths from used polishes has been investigated by using a chemical vapor transport method *via* the formation of vapor complexes RAl_nCl_{3+3n} (R = rare earth). The used polishes were chlorinated with $N_2 + Cl_2$ gas mixture at 1273 K, and the resulting rare earth chlorides were transported chemically with the vapor complexes along the temperature gradient. Most rare earth chlorides, $AlCl_3$, and $FeCl_3$ were transported during 82 hours of heating. The rare earth chlorides were mainly condensed over the temperature range of 1220 to 730 K. On the other hand, $AlCl_3$ and $FeCl_3$ were deposited at temperatures below 400 K. The highest $LaCl_3$ and $CeCl_3$ purity of about 80 pct was obtained in the process.

I. INTRODUCTION

IN recent years, rare earth elements have found applications in permanent magnets, phosphors, and hydrogen storage alloys, and their demand has been increasing every year. However, rare earth concentrates or ores occur in only limited countries and are currently imported by several countries. For a good supply of rare earths, sludge, scrap, and wastes are noted as new sources. Development of recovery processes of rare earths from them is expected. Used rare earth oxide polish is one of the wastes that can be recycled. Significant amounts of rare earth oxide mixtures are used as polishing agents for glass substrates.[1,2] The Japanese glass industry uses 2000 tons per year of the polishes, and a large portion of them is thrown away after their polishing lifetime. An efficient recovery process of rare earths from used polishes is needed in terms of recycling of the waste. Wet processes, which have been industrially used for extraction of rare earths from ores and concentrates, are proposed as recovery processes of rare earths from used polishes. However, these processes require a number of complicated treatments, such as acidolysis, alkali fusion, precipitation, and calcination, and a large quantity of waste water is discharged in these processes. Therefore, more efficient and environmentally harmless separation processes are required. On the other hand, chlorination and carbochlorination processes have been found to be effective for recovering valuable metals from scrap.[3,4,5] In these processes, valuable metals are converted to their corresponding chlorides and then separated based on the difference in volatility between the metal chlorides. It is difficult to apply this process to extract and separate rare earths, because rare earth chlorides are less volatile and can be hardly separated from other less volatile metal chlorides, especially from alkaline earth chlorides. Chlorination extraction of rare earths requires considerably high temperatures and long reaction times. In addition to that, rare earth elements have similar chemical properties to each other, and their mutual sepa-

ration is quite difficult. Rare earth chlorides also have very similar volatility. Mutual separation of rare earths is not expected in the chlorination processes. Application of the chlorination processes to rare earth separation requires an increase in apparent vapor pressure of rare earth chlorides. It has been reported that rare earth chlorides form vapor complexes with alkali chlorides and aluminum chloride:[6,7]

$$RCl_3 \ (s, \ l) + KCl \ (s, \ l) = KRCl_4 \ (g) \qquad [1]$$

$$RCl_3 \ (s, \ l) + n/2 \ Al_2Cl_6 \ (g)$$
$$= RAl_nCl_{3+3n} \ (g) \ (n = 1 \ \text{to} \ 4) \qquad [2]$$

where R denotes rare earth elements. The apparent vapor pressure of rare earth chlorides is enhanced by formation of vapor complexes. In the presence of 1 atm of Al_2Cl_6 (g), volatility enhancement of $NdCl_3$ at 600 K was calculated to be about 10^{13}.[7] Rare earth chlorides, which have low volatility, are transported chemically from higher temperature to lower temperature. We have carried out extraction of rare earths from concentrates, such as monazite, zenotime, and bastnesite,[6,8–10] and mutual separation of rare earth elements by using a dry chemical vapor transport process mediated by vapor complexes.[6,11–13] Direct extraction of rare earths from these concentrates is possible, as chlorination and chemical transport are performed simultaneously. Rare earths are separated depending on the difference in formation-dissociation equilibrium of vapor complexes. In Pr-Nd and Y-Er binary systems, comparable mutual separation efficiency to that of solvent extraction was obtained.

In this work, chlorination of used polishes with Cl_2-N_2 gas mixture is investigated, and extraction of rare earths from the polishes and mutual separation of the rare earths by a dry chemical vapor transport process were attempted.

II. EXPERIMENTAL

A. Materials

Used polish was provided by Mitsui Mining and Smelting Co., Ltd. (Tokyo, Japan) and dried at 373 K to constant weight prior to the experiment. The composition of the used polish is given in Table I. The main component of the polish is light rare earth elements, La, Ce, Pr, and Nd. It also

TETSUYA OZAKI, Graduate Student, KEN-ICHI MACHIDA, Associate Professor, and GIN-YA ADACHI, Professor, are with the Department of Applied Chemistry, Faculty of Engineering, Osaka University, Osaka 565-0871, Japan.

Table I. Composition of the Used Polish (Weight Percent)

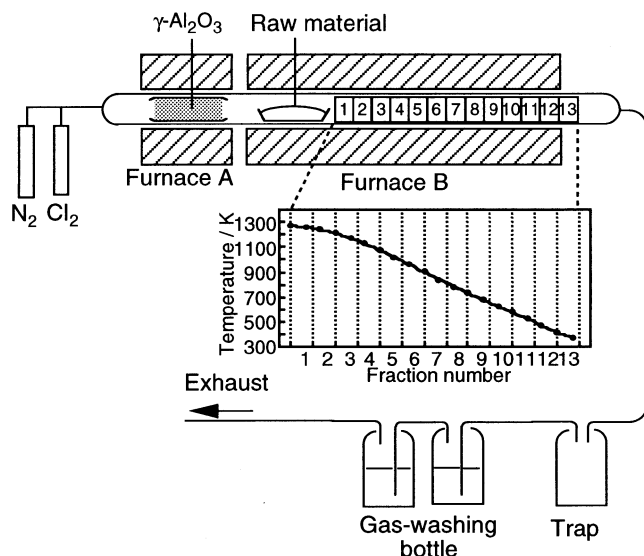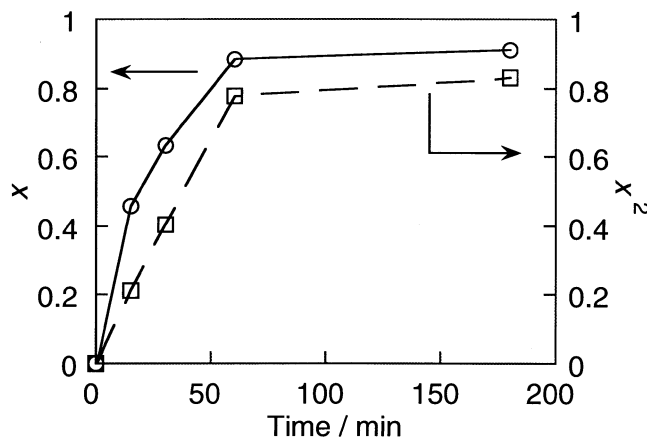| La$_2$O$_3$	CeO$_2$	Pr$_6$O$_{11}$	Nd$_2$O$_3$	CaO	SrO	Fe$_2$O$_3$	SiO$_2$	P$_2$O$_5$	SO$_3$	F
28	38	3.8	10	1.3	0.46	0.18	1.7	1.7	2.2	12

Fig. 1—CVT apparatus.

Fig. 2—Plot of x, extent of reaction, and x^2 vs time.

contains Si, Ca, Sr, Fe, F, P, and S. The X-ray powder diffraction pattern showed that the rare earths exist as oxides or oxyfluorides, while SiO$_2$ was amorphous.

B. Experimental Apparatus and Procedures

A flow type reactor with various temperature gradients was employed for the chemical vapor transport process (Figure 1). Details of the apparatus were described elsewhere.[12] The apparatus consists of two horizontal tube furnaces A and B and quartz reactor tube. Furnace B was devised for producing different kinds of temperature gradients, while furnace A was used to generate gaseous Al$_2$Cl$_6$ as the complex former. The raw material was loaded on a graphite boat, and the boat was introduced into the reactor. Inside the reactor tube, 13 pieces of quartz inner tubes were put side by side next to the boat for recovery and analysis of deposits.

The chlorination behavior was realized using a mixture of 0.5 g of the used polish and 0.5 g of active carbon as a raw material. The mixture was heated to 1273 K under the N$_2$-Cl$_2$ mixed gas flow. The flow rates of N$_2$ and Cl$_2$ were 30 to 50 and 5 mL/min, respectively. Metal components contained in the polish were gradually chlorinated by Cl$_2$, active carbon acting as a deoxidant. After 0.25 to 82 hours of chlorination reaction, the chlorinated sample was dissolved in deionized water. The resulting metal chloride, which is soluble in water, was analyzed by X-ray fluorometry, and the insoluble residue was dried, calcined to remove excess active carbon, and weighed.

The general procedure of chemical vapor transport (CVT) experiment is similar to that of the chlorination experiment, but aluminum chloride Al$_2$Cl$_6$ was used as the complex former in the experiment. Al$_2$Cl$_6$ was generated by chlorination of γ-Al$_2$O$_3$ with active carbon at 573 to 1023 K in furnace A. As treated later, it takes about an hour to chlorinate a large portion of the raw material. After heating the raw material for 2 hours, Al$_2$Cl$_6$ was introduced into the reactor to avoid reaction between rare earth oxide and Al$_2$Cl$_6$ and resulting formation of Al$_2$O$_3$ on the surface of sample.

$$R_2O_3 + Al_2Cl_6 \rightarrow 2RCl_3 + Al_2O_3 \qquad [3]$$

Rare earth chlorides react with aluminum chloride to form vapor complexes according to Eq. [2]. The vapor complexes are transported chemically along the temperature gradient from higher temperature to lower temperature, and rare earth chlorides, formed by the reverse reaction of Eq. [2], are deposited. Deposits in the reactor were recovered from every inner tube, and the metal chlorides contained in deposits and the residue were determined by the X-ray fluorescent spectrometry method with ZnCl$_2$ as internal standard.

III. RESULTS AND DISCUSSION

A. Kinetics of Chlorination of Used Polish

Figure 2 shows the percentage weight loss during chlorination of the used polish at 1273 K. More than 80 pct of the sample was chlorinated within 1 hour. However, chlorination of the remaining portion proceeded quite slowly after that, and the weight loss after 82 hours was 93.2 pct. This result suggests that components, which are hard to chlorinate, exist in the sample. The X-ray diffraction pattern of the used polishes without any treatment shows peaks assigned to rare earth oxide and oxyfluoride, while that of the sample after chlorination for 1 hour shows only peaks of rare earth fluoride (Figure 3). It seems that the chlorinated residue mostly consists of rare earth fluoride. Equations [4] and [5] have been proposed as the reaction scheme for chlorination of Ln$_2$O$_3$ and CeO$_2$, respectively.

$$Ln_2O_3 + 2C + 3Cl_2 \rightarrow 2LnCl_3 + 3CO \qquad [4]$$

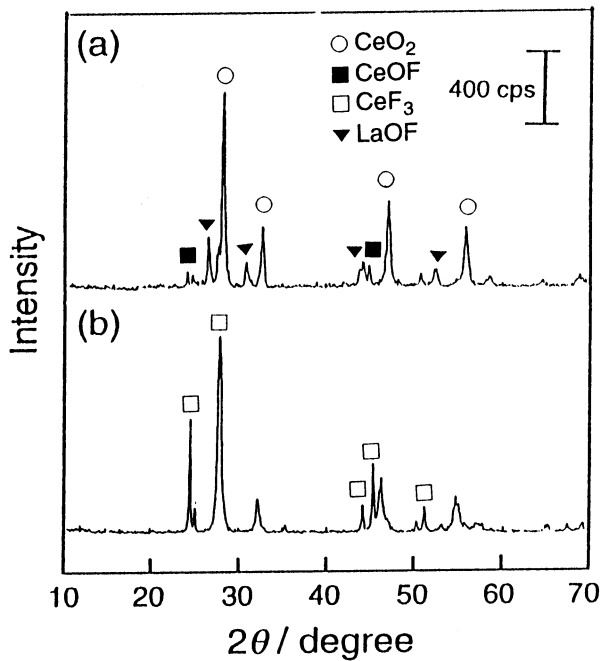$$2CeO_2 + 4C + 3Cl_2 \rightarrow 2CeCl_3 + 4CO \qquad [5]$$
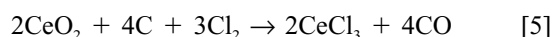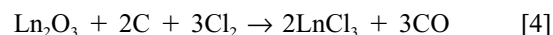
Fig. 3—The X-ray diffraction pattern of (*a*) original used polish and (*b*) solid residue from the chlorination for 1 h.
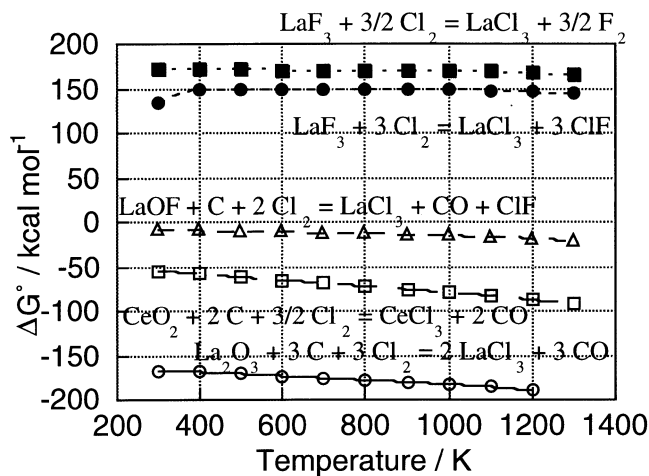

Fig. 4—Gibbs energy change for chlorination reaction of La_2O_3, CeO_2, LaOF, and LaF_3 as a function of temperature.
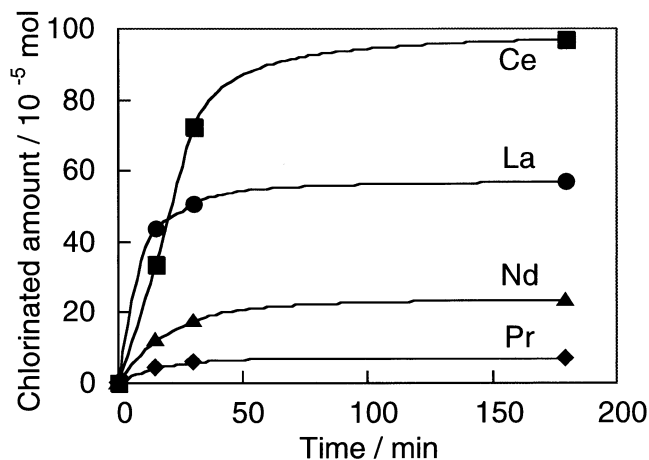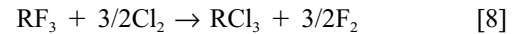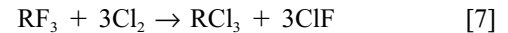

Fig. 5—Chlorinated molar quantity of rare earth components.

And we concluded in previous work that the most plausible reaction scheme for chlorination of rare earth oxyfluorides was[9]

$$LnOF + C + 2Cl_2 \rightarrow LnCl_3 + CO + ClF \qquad [6]$$

On the other hand, Eqs. [7] and [8] are expected for the reaction scheme of chlorination of rare earth fluorides.

$$RF_3 + 3Cl_2 \rightarrow RCl_3 + 3ClF \qquad [7]$$

$$RF_3 + 3/2Cl_2 \rightarrow RCl_3 + 3/2F_2 \qquad [8]$$

The Gibbs free energy changes of these reactions are shown in Figure 4 as a function of temperature from 273 to 1273 K.[15,16,17] These thermodynamic values indicate that the chlorination of La_2O_3, CeO_2, and LaOF with Cl_2 are thermodynamically feasible in the presence of carbon between 273 and 1273 K, and that chlorination of LaF_3 is not thermodynamically favorable in the same temperature range. Therefore, rare earth oxides and oxyfluorides are rapidly chlorinated, while it is difficult to chlorinate rare earth fluorides. The result of X-ray florescence spectrometry suggests that SiO_2 as well as rare earth fluorides remained in the residue. The following equation was found to hold for chlorination of the used polish for chlorinating time within 1 hour:

$$kt = x^2 \qquad [9]$$

where k = constant, t = chlorination time (min), and x = extent of reaction. This equation was applied for a gas-solid reaction of the sample with the shape of flat plate controlled by pore diffusion.[18] We previously investigated chlorination of monazite with carbon tetrachloride, and the data of the chlorination rate are best fitted to Eq. [10], which describes a reaction of a spherical sample controlled by the chemical reaction[9]

$$kt = 1 - (1 - x)^{1/3} \qquad [10]$$

However, the sample used in the present work has small particle size and high density, and its shape is regarded as flat plate. It is impossible to fit the chlorination rate of used polish to one equation, and detailed consideration for the reaction is difficult because of the existence of a sparingly chlorinated portion in it. In the discussion, this portion is neglected.

Figure 5 shows the chlorinated amount of each rare earth element contained in the polish. The chlorination rate of the rare earths increases according to the following order:

$$La > Pr > Nd > Ce \qquad [11]$$

It has been reported that the chlorination rate of rare earths generally decreases with increasing atomic number. However, this is not applicable to Ce. Chlorination of Ce is much slower than that of Pr and Nd, because the chlorination of CeO_2 was accompanied by the reduction from Ce (IV) to Ce (III). The Gibbs free energy change of both the chlorination reactions (Figure 4) also supports the experimental result that CeO_2 is less subject to chlorination by chlorine than La_2O_3.

B. *Transport Efficiency of Rare Earth Chlorides*

Transport efficiency of rare earth chlorides by chemical vapor transport using $AlCl_3$ as the complex former was in-
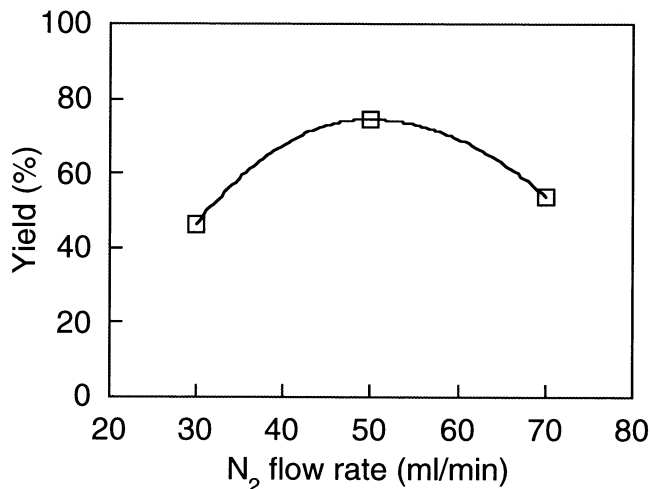
Fig. 6—Effect of N$_2$ flow rate on the yield of rare earth chlorides.

Table II. The Yields of Rare Earth Chlorides for CVT Experiments with Various Temperature of Furnace A

Temperature of Furnace A/K	Yields/Pct				
	Total	La	Ce	Pr	Nd
573	74	59	84	84	81
773	82	65	89	93	87
873	75	57	83	86	82

vestigated in different transport conditions. The total deposited amount yield of rare earth chlorides was defined as follows:

$$\text{Yield (pct)} = N_{\text{total}}/(N_{\text{total}} + N_{\text{boat}}) \times 100 \qquad [12]$$

where N_{total} and N_{boat} are the molar quantity values of the total transported rare earth chloride and the residual rare earth chloride in the boat, respectively. The transported amount consists of solely evaporated amount and chemically transported amount *via* the vapor complexes. Both partial pressure of complex former Al$_2$Cl$_6$ and flow rate of carrier gas N$_2$ affect the amount of formed vapor complexes. The effect of gas flow rate on the transport efficiency was investigated. The effect of reaction temperature of furnace A, where gaseous Al$_2$Cl$_6$ was generated, on the transport efficiency was also investigated. Figure 6 shows the relationship between transported amount of rare earth chloride and N$_2$ flow rate with constant Furnace A temperature of 573 K. The transported amount passes through a maximum at about 50 mL/min. When the N$_2$ flow rate is too large, partial pressure of AlCl$_3$ decreases and the amount of vapor complexes formed also decreases.

Table II summarizes the yields of rare earth chlorides at the various temperatures of furnace A with 50 mL/min of N$_2$ flow rate. Amount of AlCl$_3$ generated increases with increasing reaction temperature. It seems that the larger the introduced amount of AlCl$_3$, the larger is the amount of vapor complex formed. However, excess AlCl$_3$ inhibited vaporization and chemical transport of rare earth chlorides because of formation of alumina layer on the surface of samples by reaction of AlCl$_3$ and rare earth oxides (Eq. [3]).

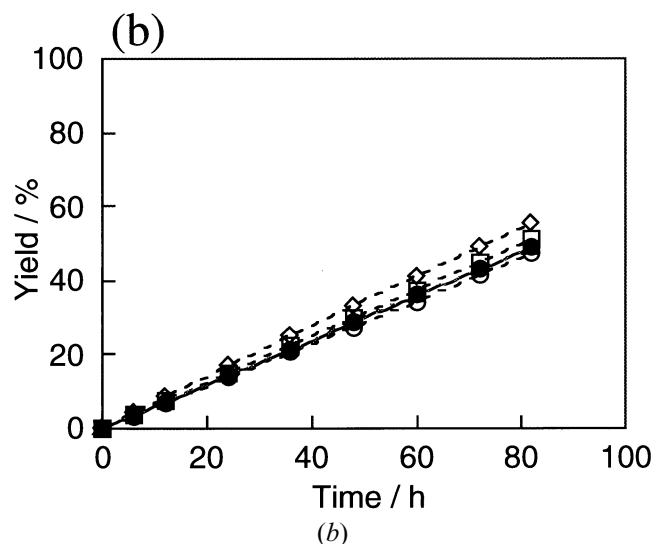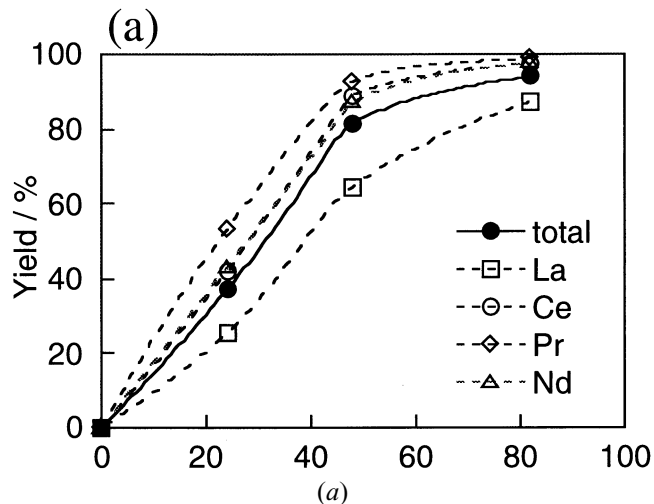The highest yield was obtained when N$_2$ flow rate was 50 mL/min and temperature of furnace A was 773 K.

Fig. 7—(*a*) Yields of rare earth chlorides under the optimized CVT condition as a function of time and (*b*) that calculated from thermodynamic data.

Therefore, the CVT experiments after this were performed with these transport conditions. Yields of total and each rare earth chloride *vs* time curves are shown in Figure 7(a). The yield of rare earth chloride totaled 94 pct after CVT experiment for 82 hours. Transport reaction rate of rare earth chlorides increased according to the following order:

$$\text{LaCl}_3 < \text{NdCl}_3 < \text{CeCl}_3 < \text{PrCl}_3 \qquad [13]$$

In the RCl$_3$-AlCl$_3$ (R = La-Nd) systems, it was found that the dominant vapor complex species is RAl$_3$Cl$_{12}$. Gibbs energy changes for Eq. [14] at 1273 K,

$$\text{RCl}_3 \text{ (s, 1)} + 3/2\text{Al}_2\text{Cl}_6 \text{ (g)} = \text{RAl}_3\text{Cl}_{12} \text{ (g)} \qquad [14]$$
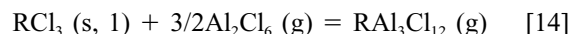
are 38.0, 39.0, 36.7, and 38.8 kJ mol^{-1} for R = La, Ce, Pr, and Nd, respectively.[19] The equilibrium constant K_p for Eq. [14] is

$$K_p = P_{\text{RAl3Cl12}}/(P_{\text{Al2Cl6}})^{3/2} \qquad [15]$$

Where P_{RAl3Cl12} and P_{Al2Cl6} are partial pressures of RAl$_3$Cl$_{12}$ and Al$_2$Cl$_6$, respectively. When N$_2$ gas flow rate was 50 mL/min and the temperature of furnace A was 773 K, the vapor pressure of Al$_2$Cl$_6$ was calculated to be 6.38×10^{-2}
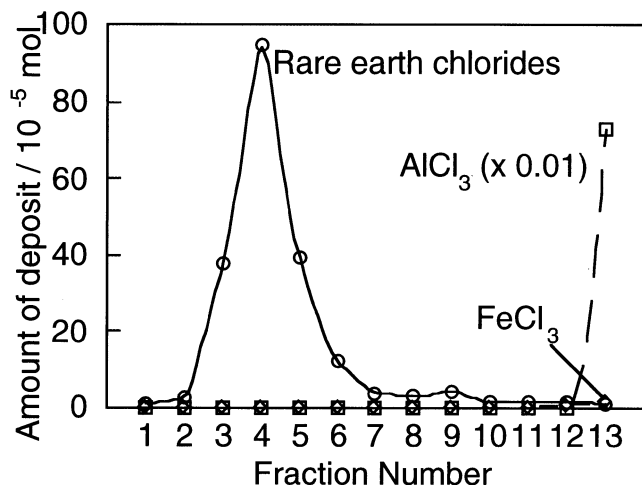
Fig. 8—Distribution of metal chloride deposits under linear gradient.

atm from weight loss of γ-Al_2O_3 in furnace A. The K_p value was calculated with previously described Gibbs energy changes and the relationship

$$\Delta G = RT \ln K_p \qquad [16]$$

where R is the gas constant and T is the reaction temperature. The molar fraction of La, Ce, Pr, and Nd in the raw material was 0.34, 0.49, 0.047, and 0.12, respectively. If the composition of each rare earth was maintained after chlorination, the partial pressure of each vapor complex could be expressed approximately by the following equation:

$$P'_{RAl3Cl12} = x_R \cdot P_{RAl3Cl12} \qquad [17]$$

where x_R is the molar fraction of the rare earth element. The transported amount of rare earth chlorides *via* vapor complexes with Al_2Cl_6 was obtained using the ideal gas equation:

$$n_R = PV/RT = P'_{RAl3Cl12} \cdot (10^{-6} \cdot V_{N2} \cdot t)/RT \qquad [18]$$

where V_{N2} is N_2 gas flow rate (mL/min) and t is reaction time (minutes). Figure 7(b) shows the calculated yields of rare earth chlorides. A large difference was observed between the experimental and calculated values. This deviation may arise from the following factors. First, the effect

of a solely vaporized amount of rare earth chlorides is not negligible at 1273 K. Indeed, the vapor pressure of rare earth chlorides itself is much lower than that of vapor complexes with Al_2Cl_6 at relatively low temperatures. However, the volatility enhancement by formation of a vapor complex is small at temperatures higher than 1000 K. In the present work, because the partial pressure of Al_2Cl_6 is not so high, a considerable amount of rare earth chlorides may vaporize and transport to lower temperature regions simultaneously with the CVT reaction. The kinetic factor also affects the transport efficiency. As the complexation reaction between rare earth chloride and aluminum chloride is a gas-solid reaction, it is impossible to explain the reaction completely by equilibrium, and density and shape of sample also affect the reaction. The chemical transport rate of each rare earth chloride is larger than the calculated value. The differences in stability of vapor complexes between rare earths estimated from thermodynamic data are small. So these differences are based on the differences in volatility of rare earth chlorides or the kinetic factor.

C. Extraction of Rare Earths from Used Polish

Two kinds of temperature gradients were adopted in the chemical vapor transport experiments. Recovery of rare earths from used polish was investigated with an almost linear temperature gradient of 28 K cm^{-1} (Figure 1). Distributions of deposition of rare earth chloride and other metal chlorides *vs* the fraction number (*FN*) with optimized transport condition obtained in the preceding section and reaction time of 82 hours are shown in Figure 8, and the transported amount of metal chlorides in each fraction is shown in Table III. Rare earth chlorides are mainly deposited in *FN* = 3 to 8 (1220 to 730 K). The purity of the rare earth chlorides in the temperature range was about 95 pct. Volatile metal chlorides, $AlCl_3$ and $FeCl_3$, were deposited at *FN* = 13 (<400 K), and nonvolatile alkaline earth chlorides, $SrCl_2$ and $CaCl_2$, were scarcely transported and remained in the residue. Other elements contained in the polishes, such as Si, remained in the residue as an oxide. It was found that rare earth chlorides were almost completely separated from other metal chlorides by using $AlCl_3$ as a complex former, and that recycling of $AlCl_3$ was also possible by removing a small amount of $FeCl_3$.

Table III. Transported Amount of Metal Chlorides

| FN	Temperature Range/K	Amount of Deposit/10^{-5} Mol							
		La	Ce	Pr	Nd	Al	Fe	Sr	Ca
1	1273 to 1260	0.40	0.94	0.19	0.31	0	0	0	0
2	1260 to 1220	0.37	0.67	0.06	0.17	0	0	0	0
3	1220 to 1160	6.18	14.71	1.11	3.35	0	0	0	0.09
4	1160 to 1080	5.88	22.90	1.52	4.69	0	0	0	0.19
5	1080 to 990	1.07	6.21	0.46	1.05	0	0	0	0
6	990 to 900	0.33	2.19	0.24	0.34	0	0	0	0
7	900 to 820	0.21	1.71	0.20	0.29	0	0	0	0
8	820 to 730	0.44	1.26	0.23	0.37	0	0	0	0
9	730 to 650	0.13	0.20	0.12	0.10	0	0	0	0
10	650 to 570	0.19	0.58	0.17	0.24	7.93	0	0	0
11	570 to 490	0.12	0.18	0.18	0.13	19.25	0.10	0	0
12	490 to 400	0.16	0.23	0.16	0.13	16.95	0.80	0	0
13	400 to 330	0.20	0.49	0.07	0.11	528.53	1.56	0	0
Boat	—	13.08	3.51	0.02	0.71	7.62	2.90	0.16	3.02
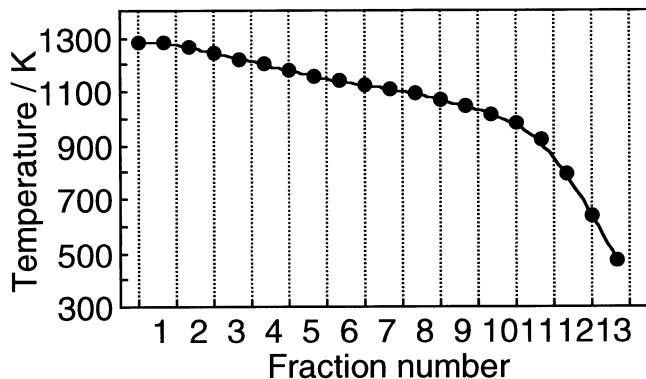
Fig. 9—Temperature gradient with smaller gradient (10 K cm⁻¹).
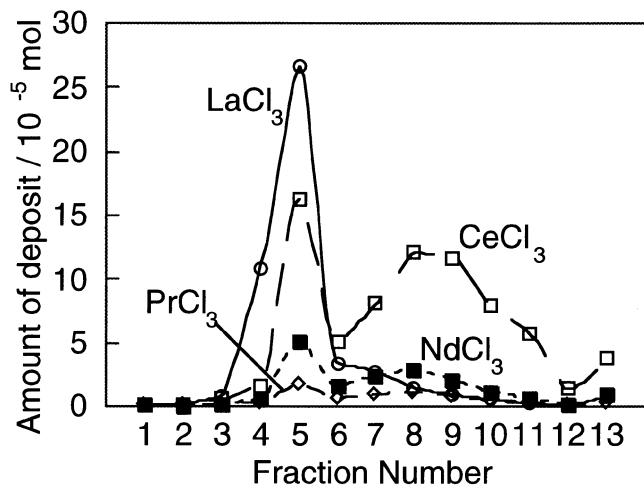

Fig. 10—Distribution of rare earth chloride deposits under smaller gradients.

D. *Mutual Separation Characteristics of Rare Earths*

Mutual separation efficiency between rare earth elements in the polish was studied by chemical vapor transport experiment under the smaller temperature gradient (10 K cm⁻¹) (Figure 9). The distribution of deposits of rare earth chlorides under the smaller temperature gradient was shown in Figure 10. While $LaCl_3$ was mainly deposited in $FN =$ 3 to 6 (1240 to 1120 K), $CeCl_3$ was deposited in $FN = 6$ to 12 (1120 to 640 K). $PrCl_3$ and $NdCl_3$ were deposited in the whole region of the temperature gradient. More than 80 pct of purity was obtained for $LaCl_3$ and $CeCl_3$ at higher and lower temperature regions, respectively. To evaluate the mutual separation efficiency between two elements, we defined separation factors as follows:

$$\beta_{R/R'} = (N_{HR}/N_{HR'})/(N_{0R}/N_{0R'}) \qquad [19]$$

$$\beta_{R'/R} = (N_{LR'}/N_{LR})/(N_{0R'}/N_{0R}) \qquad [20]$$

where N_{HR} and N_{LR} are the molar quantities of the deposits transported to high- and low-temperature sides, respectively, and N_{OR} and $N_{OR'}$ are R and R' contents of the initially loaded raw mixture. Table IV shows the separation factors between any two rare earth elements contained in the used polish. Favorable mutual separation efficiency was

Table IV. Separation Factors $\beta_{R/R'}$ under Smaller Temperature Gradient

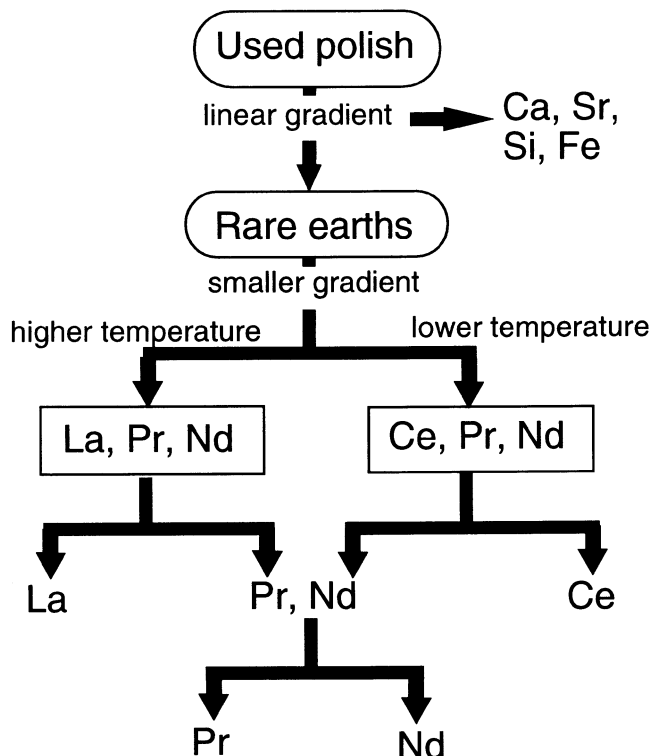|	R'		
R	Ce	Pr	Nd
La	4.47	2.07	2.22
Ce	—	1.31	1.32
Pr	—	—	1.01

Fig. 11—Proposed flow sheet for the recovery of rare earths from used polish.

obtained for the La/Ce pair. The separation factor between them was 4.47. The separation factor values for (La, Ce)/(Pr, Nd) pairs were in the range of 1.3 to 2.3. It has been shown that, when two rare earth chlorides are completely transported, separation factor between them is constant and independent of the ratio. Therefore, if the separation factor in a binary system is larger than 1, mutual separation improves in the system by repetition of the process. $LaCl_3$ and $CeCl_3$ are expected to be separated almost completely by repeating this process more than four times. More repetition makes it possible to separate $LaCl_3$ or $CeCl_3$ from a mixture of $PrCl_3$ and $NdCl_3$. On the other hand, $PrCl_3$ and $NdCl_3$ were hardly separated from each other. However, Murase *et al.*[13] have presented that mutual separation efficiency as high as solvent extraction process was obtained for the Pr-Nd binary system in the CVT process by introducing temperature gradients with a constant-temperature plateau zone. Therefore, mutual separation of rare earths is possible according to the flow sheet shown in Figure 11.

V. CONCLUSIONS

1. Most of rare earth oxides and oxyfluorides in the used polish are chlorinated under N_2-Cl_2 stream within an hour. However, it is difficult to chlorinate the polish completely because it contains rare earth fluorides, which are hardly subject to chlorination. The reaction rate of chlorination follows the relation $kt = x^2$.
2. Rare earth chlorides formed by chlorination of the used polish are transported chemically along the temperature gradient *via* gaseous complex with aluminum chloride. Deposition of rare earth chlorides is scarcely overlapped with that of other metal chlorides. It is possible to extract rare earths from the used polish by chemical vapor transport process.
3. The yield of the rare earths depends on the N_2 gas flow rate and partial pressure of Al_2Cl_6. The difference in transport rate of the rare earth chlorides is not based on stability of the vapor complexes but on kinetic factor and volatility of the rare earth chloride itself.
4. Mutual separation between rare earth chlorides based on the difference in formation-dissociation equilibrium of vapor complexes is possible. Satisfactory separation characteristics are obtained especially between La and Ce.

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