Comparative Study of the Mutual Separation Characteristics and Mechanism for Neighboring Rare-Earth Elements from Binary Chloride Mixtures and Oxide Mixtures via Vapor Complexes

Zhi-Chang Wang,* Jin Yu, and Yong-Li Yu

Department of Chemistry, Northeastern University, Shenyang 110006, Liaoning, China

(Received November 27, 1995)

A comparative study of the mutual separation characteristics and mechanism was made for neighboring rare-earth elements La, Ce, Pr, and Nd from their binary chloride mixtures and oxide mixtures using a chemical vapor-transport reaction under a suitable temperature and pressure gradient. The separation factors, expressed as the atomic ratios for the resulting chlorides, were observed within 6 h up to 21.4 for La : Ce, ⩾100 for Pr : Ce, and 1.84 for Pr : Nd from the oxide mixtures; however, they were only 12.3 for La : Ce, 5.79 for Pr : Ce, and 1.32 for Pr : Nd from the chloride mixtures under identical reaction conditions, using $AlCl_3$ as the sole complex former. It was also observed for the mutual separation from the oxide mixtures that the separation factors increased when KCl was added as another complex former, but decreased several times when either without chlorine in the carried gas, or without active carbon in the raw material, or under a poor vapor-transport condition. These results provide evidence that this reaction for the oxide mixtures would mainly be the combination of a carbothermic reduction-chlorination of the oxides, complexation of the chlorides, and transportation of the vapor complexes.

Rare earths play an important role in the field of advanced materials science. At present, rare-earth separation and purification for commercial use are mainly carried out using solvent extraction and ion-exchange chromatography. These wet processes, however, require not only complicated treatments, but also many repeated operations, especially for mutual separation between such neighboring rare-earth elements as Pr and Nd. Thus, not surprisingly, a search for new processes with a degree of efficiency, selectively and generality for rare-earth separation lies at the center of rare-earth chemistry.

Rare-earth chlorides may react with other chlorides, forming such vapor complexes as $LnAl_nCl_{3n+3}$[1—7] and $ALnCl_4$,[8—11] where Ln = rare-earth elements and A = alkaline metal elements. Very recently, Adachi and co-workers[12—16] successfully developed a chemical vapor-transport process for the mutual separation of rare-earth elements mediated by vapor complexes. The reported separation factors, expressed as atomic ratios for the resulting chlorides, within 6 h from binary chloride mixtures, were 10.8 for Pr : Er,[15] 2.3 for Pr : Sm,[15] and 1.07 for Nd : Pr,[13,14] using $AlCl_3$ as a complex former, or 1.04—1.13 for Pr : Nd[13,14] and 1.16—1.33 for Nd : Pr,[13,14] using ACl or $AlCl_3$–ACl mixture as a complex former. They have also reported separation results within 12 h from a ternary chloride mixture, $PrCl_3$–$GdCl_3$–$ErCl_3$,[15] using $AlCl_3$ as a complex former, and within 82 or 84 h from a monazite concentrate and its crude oxide,[16] using KCl and $POCl_3$ as complex formers. Their experimental results provide evidence that this dry process has many advantages over the conventional wet processes, and that by using the dry process rare earths can be mutually separated not only from their chloride mixtures within 6 or 12 h, but also from their oxide mixtures within 82 or 84 h. This dry process has also been used as a powerful tool for the recovery of rare earths from sludges of Sm_2Co_{17},[17,18] $Nd_2Fe_{14}B$,[18] and $LaNi_5$[18] intermetallic materials.

Both a high separation factor and a short reaction time would be required for a potential industrial process. Questions therefore raise concerning the chemical vapor-transport process for rare-earth separations: whether the mutual separation between neighboring rare earths from their oxide mixtures can also be realized only within 6 h, which one is the more efficient raw material (a chloride mixture or an oxide mixture) and which one is the more efficient complex former for rare-earth oxide mixtures ($AlCl_3$ or an $AlCl_3$–ACl mixture). In this work, we tried to make a comparative study of the mutual-separation characteristics for neighboring rare-earth elements La, Ce, Pr, and Nd from their binary chloride mixtures and binary oxide mixtures using the chemical vapor-transport reaction under a definite reaction condition.

Experimental

The chemicals used in this study were of analytical purity for anhydrous $AlCl_3$ and NH_4Cl, 99.95% purity for $CeCl_3 \cdot 7H_2O$, and ⩾99.9% purity for La_2O_3, CeO_2, Pr_6O_{11}, and Nd_2O_3. Anhydrous $AlCl_3$ was further purified by careful sublimation in a vacuum. Anhydrous rare-earth chlorides ($LaCl_3$, $CeCl_3$, $PrCl_3$, and $NdCl_3$) were prepared by the reactions of La_2O_3, $CeCl_3 \cdot 7H_2O$, Pr_6O_{11}, and Nd_2O_3 with a large excess of NH_4Cl at 520—570 K in a vacuum; finally, the residual NH_4Cl was removed at 670 K in a vacuum.

The chemical vapor-transport reaction was carried out in a cylindrical alumina reactor tube, 25 mm in inner diameter and 1000 mm in length, with a given temperature and pressure gradient, as shown in Fig. 1; the temperature gradient was very similar to that used by Adachi and co-workers.[12—18] A mixture of dry Cl_2 gas and dry N_2 gas with flow rates of 15 and 40 cm^3 min^{-1}, respectively, was introduced from the inlet of the reactor tube, and the pressure gradient was maintained by a subatmospheric pressure of 2.7 kPa at its outlet. Anhydrous aluminum chloride was sealed in a glass ampul with a small hole, and placed at 473 K near to the inlet of the reactor so as to control its evaporation rate. A raw material was formed by mixing active carbon with either a rare-earth compound at an atomic ratio of C : Ln = 7.5 : 1, or a binary mixture at an atomic ratio of C : Ln : Ln′ = 15 : 1 : 1, and then placed into a graphite boat and kept at 1300 K. Seventeen pieces of short alumina tubes, each being 17 mm in inner diameter and 25 mm in length and acting as a receptor, were placed side by side at temperatures from 1300 K to 400 K along the inner wall of the reactor. At the end of each run, the produced anhydrous rare-earth chlorides were collected in all seventeen receptors due to their low volality, while the reproduced anhydrous aluminum chloride was deposited only in the last few receptors at low temperature near to the outlet of the reactor, due to its high volatility. The amounts of rare-earth chlorides produced were then determined from the peak intensity of the characteristic bands[19] (333.75 nm for La^{3+}, 418.66 nm for Ce^{3+}, 422.54 nm for Pr^{3+}, and 406.11 nm for Nd^{3+}) using an inductively coupled plasma atomic emission spectrometer (Allied Analytical Systems ICP-Plasma 200).

Results and Discussion

Figure 2 shows the reaction results of four pure chlorides [$LaCl_3$ (Fig. 2A), $CeCl_3$ (Fig. 2B), $PrCl_3$ (Fig. 2C), and $NdCl_3$ (Fig. 2D)], and four pure oxides [La_2O_3 (Fig. 2E), CeO_2 (Fig. 2F), Pr_6O_{11} (Fig. 2G), and Nd_2O_3 (Fig. 2H)] in the form of deposition profiles for the rare-earth chlorides produced vs. the fraction number (FN), where $AlCl_3$ was the sole complex former. It can be seen that the transport amount was always larger from the oxides than from the chlorides. Figure 3 compares the reaction results of the three binary chloride mixtures [$LaCl_3$–$CeCl_3$ (Fig. 3A), $CeCl_3$–$PrCl_3$ (Fig. 3B), and $PrCl_3$–$NdCl_3$ (Fig. 3C)] with those of the three binary oxide mixtures [La_2O_3–CeO_2 (Fig. 3D), CeO_2–Pr_6O_{11} (Fig. 3E), and Pr_6O_{11}–Nd_2O_3 (Fig. 3F)] in the same form, where $AlCl_3$ was also the sole complex former. It can be seen that the separation factors for La : Ce, Pr : Ce, and Pr : Nd were always larger from the oxide mixtures than from the chloride mixtures. The values of the obtained separation factors are summarized in Table 1. The value of 21.4 for La : Ce, $\geqslant 100$ for Pr : Ce, and 1.84 for Pr : Nd from the oxide mixtures would be the largest or nearly the largest ones reported for the three neighboring element pairs. Table 2 gives the values of the separation factors in the case with the largest transport amounts for the sum of the elements. Here, the values of 4.04 and 5.27 for La : Ce, 33.5 and $\geqslant 100$ for Pr : Ce, and 1.63 and 1.68 for Pr : Nd from the oxide mixtures would still be large enough and show the potential applicabilities. Besides, Fig. 3C shows the separation factor for Pr : Nd from $PrCl_3$–$NdCl_3$ to be larger than 1.12 at all fraction numbers, except for only FN = 1, 2, and 6; Adachi and co-workers,[13,14] however, reported it to be only 1.00 for Pr : Nd and 1.07 for Nd : Pr from the same system and using the same complex former. The former higher separation factor might benefit from the suitable pressure gradient in the reactor tube, higher atomic ratio of C : Ln in the raw material, and the higher flow rate of Cl_2 used in this study.

Moreover, an additional chemical vapor-transport reaction was carried out in which the raw material was formed by mixing active carbon with KCl and Pr_6O_{11}–Nd_2O_3 at an atomic ratio of C : K : Pr : Nd = 22 : 1 : 1 : 1, so that both vapor complexes $LnAl_nCl_{3n+3}$ and $KLnCl_4$ may be formed and

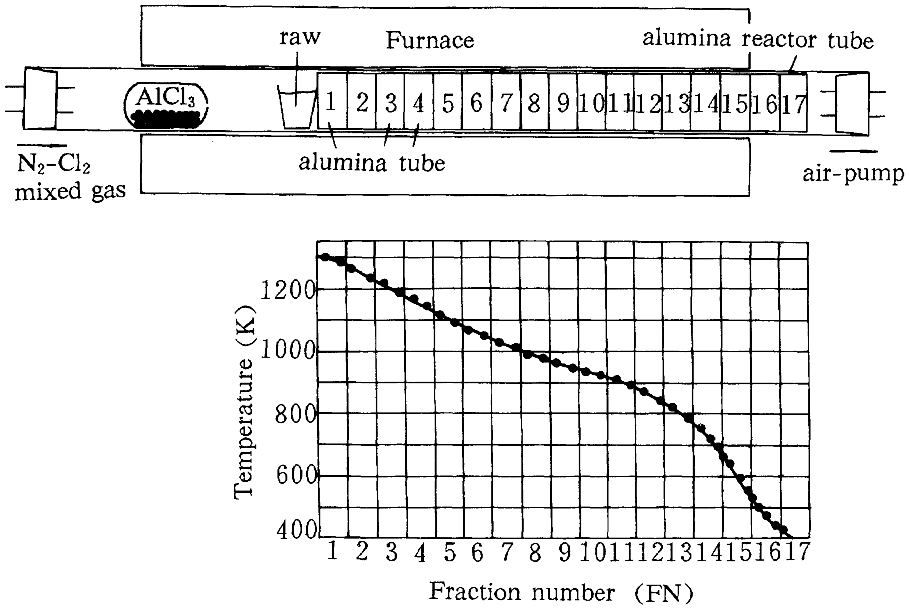

Fig. 1. A schematic representation of the reactor with a given temperature and pressure gradient for the chemical vapor transport reaction used in this study.

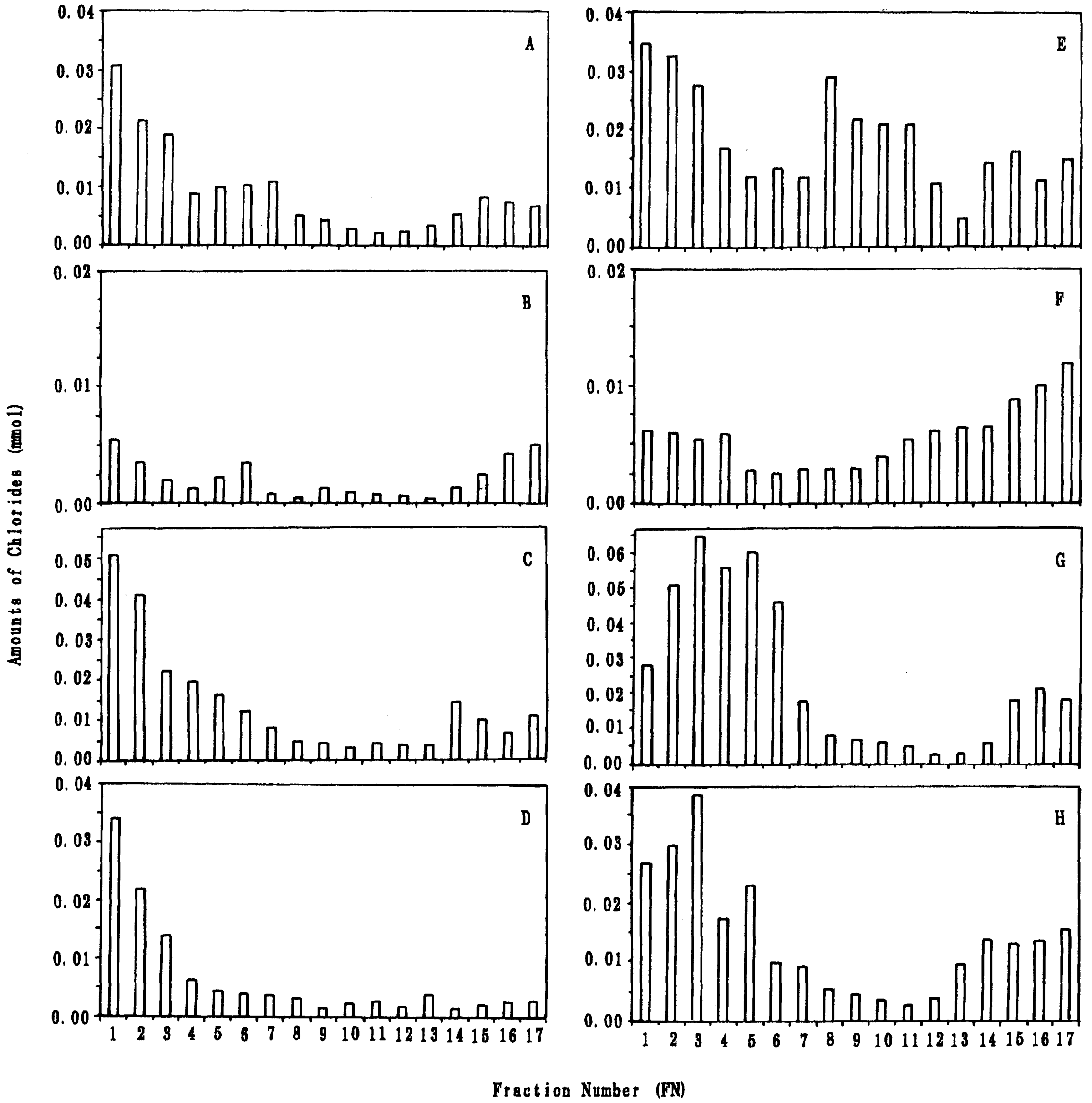

Fig. 2. Distribution of $LaCl_3$, $CeCl_3$, $PrCl_3$, and $NdCl_3$ deposits in a chemical vapor transport reaction formed from pure rare earth chlorides and oxides; (A) $LaCl_3$, (B) $CeCl_3$, (C) $PrCl_3$, (D) $NdCl_3$, (E) La_2O_3, (F) CeO_2, (G) Pr_6O_{11}, and (H) Nd_2O_3. The complex former was $AlCl_3$ and the atomic ratio in the raw materials was C : Ln = 7.5 : 1.

transported. The results are shown in Fig. 4 and Tables 1 and 2. It can be seen that the addition of KCl causes an increase in the separation factor for Pr : Nd from 1.84 to 2.09. However, the increase is still smaller than that from 1.32 to 1.84 for Pr : Nd caused by changing $PrCl_3$–$NdCl_3$ (see Fig. 3C) to Pr_6O_{11}–Nd_2O_3 (see Fig. 3F) in the raw material.

The mechanism of the chemical vapor-transport reaction for rare-earth oxides is not very clear. It may mainly be a combination of carbothermic reduction-chlorination reaction of the rare-earth oxides:

$$(1/2)Ln_2O_3(s) + (3/2)C(s) + (3/2)Cl_2(g) = LnCl_3(l) + (3/2)CO(g), \tag{1}$$

$$CeO_2(s) + 2C(s) + (3/2)Cl_2(g) = CeCl_3(l) + 2CO(g), \tag{2}$$

$$(1/6)Pr_6O_{11}(s) + (11/6)C(s) + (3/2)Cl_2(g) = PrCl_3(l) + (11/6)CO(g), \tag{3}$$

a complexation reaction of the rare-earth chlorides produced,

$$LnCl_3(l) + (n/2)Al_2Cl_6(g) = LnAl_nCl_{3n+3}(g), \tag{4}$$

and the transport of the rare-earth complexes. In the special case that the raw material was formed by mixing active carbon with KCl and rare-earth oxides, another complex may be formed by the complexation reaction

$$LnCl_3(l) + KCl(l) = KLnCl_4(g). \tag{5}$$

The total reaction may begin with the carbothermic reduction-chlorination reaction of oxides to form anhydrous rare-

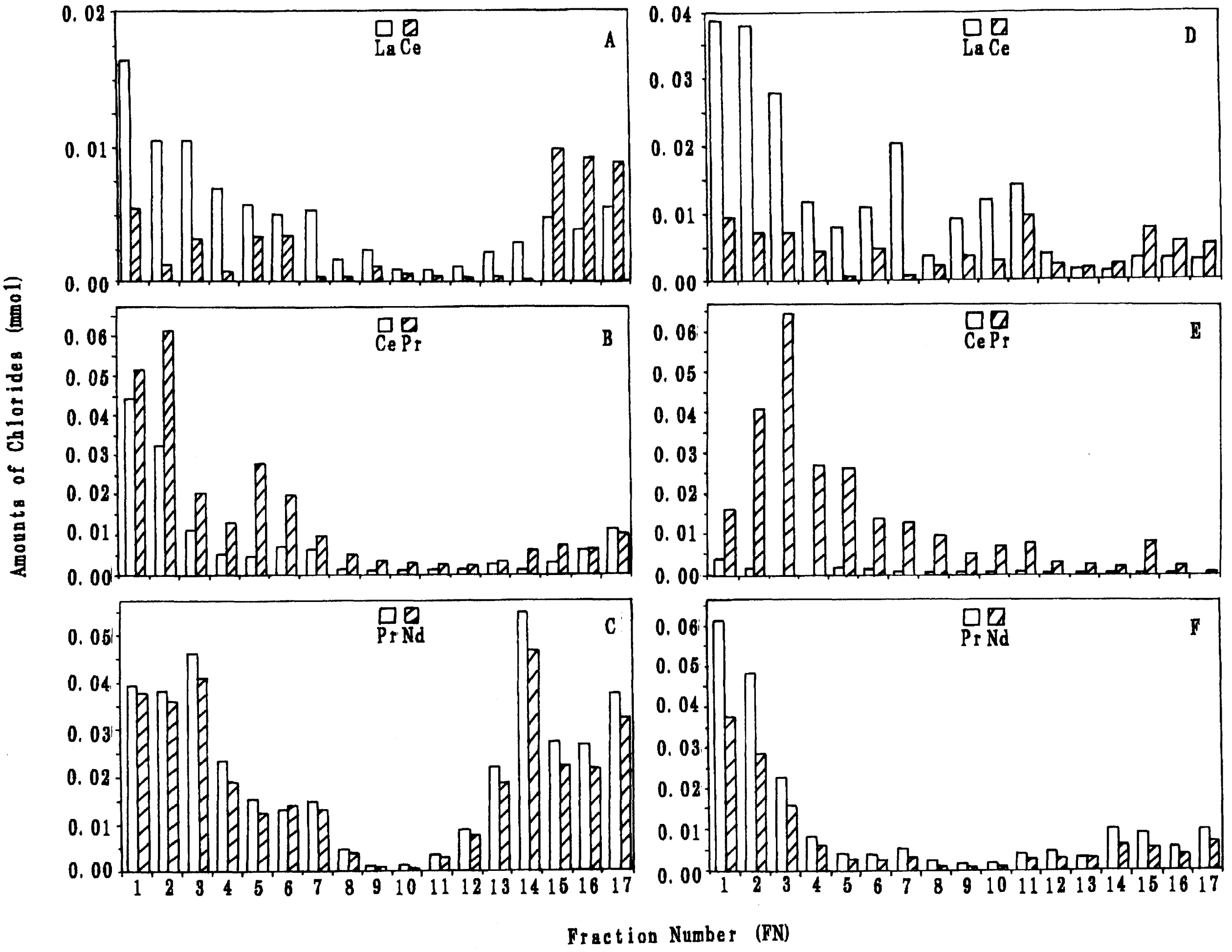

Fig. 3. Distribution of $LaCl_3$, $CeCl_3$, $PrCl_3$, and $NdCl_3$ deposits in a chemical vapor transport reaction formed from binary rare earth chloride mixtures and oxide mixtures: (A) $LaCl_3$–$CeCl_3$, (B) $CeCl_3$–$PrCl_3$, (C) $PrCl_3$–$NdCl_3$, (D) La_2O_3–CeO_2, (E) CeO_2–Pr_6O_{11}, and (F) Pr_6O_{11}–Nd_2O_3. The complex former was $AlCl_3$ and the atomic ratio in the raw materials was C : Ln : Ln′ = 15 : 1 : 1.

Table 1. The Largest Separation Factors between Neighboring Rare Earth Elements La, Ce, Pr, and Nd from Their Binary Chloride Mixtures and Binary Oxide Mixtures Using A Chemical Vapor Transport Reaction

Mixtures	SF[a)]	FN[b)]		Complex formers
$LaCl_3$–$CeCl_3$	12.3	7	(La : Ce)	$AlCl_3$
$CeCl_3$–$PrCl_3$	5.79	5	(Pr : Ce)	$AlCl_3$
$PrCl_3$–$NdCl_3$	1.32	10	(Pr : Nd)	$AlCl_3$
La_2O_3–CeO_2	21.4	7	(La : Ce)	$AlCl_3$
CeO_2–Pr_6O_{11}	$\geqslant 100$	3	(Pr : Ce)	$AlCl_3$
Pr_6O_{11}–Nd_2O_3	1.84	8	(Pr : Nd)	$AlCl_3$
Pr_6O_{11}–Nd_2O_3	2.09	6	(Pr : Nd)	$AlCl_3$and KCl

a) SF = Separation factor, b) FN = Fraction number.

earth chlorides (Eqs. 1, 2, and 3) at high temperature (1300 K). The newly formed anhydrous rare-earth chlorides may complex more easily than the prepared ones with gaseous anhydrous aluminum chloride to from the vapor complexes $LnAl_nCl_{3n+3}$ (Eq. 4) and with liquid KCl to form the vapor complexes $KLnCl_4$ (Eq. 5) at the same temperature. The vapor complexes may be chemically transported from one place at high temperature and pressure to other places at low temperature and pressure in the reactor tube according to Eqs. 4 and 5. Finally, all of the anhydrous chlorides may be reproduced by the reverse reaction of Eqs. 4 and 5, and condensed in the receptors along the transport road, since the vapor complexes were less stable at low temperature than at high temperature. In the case that the rare-earth chlorides were used as raw materials, the carbothermic reduction-chlorination reaction of the oxides (Eqs. 1, 2, and 3) disappeared. Therefore, the difference in the carbothermic reduction-chlorination reaction of the oxides might be the main reason for the more efficient separation from the oxide mixtures than from the chloride mixtures. The formation-

Table 2. Separation Factors between Neighboring Rare Earth Elements La, Ce, Pr, and Nd from Their Binary Chloride Mixtures and Binary Oxide Mixtures in the Case with Highest transport Amounts for the Sum of the Elements Using A Chemical Vapor Transport Reaction

Mixtures	SF[a)]	FN[b)]	SF[a)]	FN[b)]		Complex formers
$LaCl_3$–$CeCl_3$	3.12	1;			(La : Ce)	
	2.05	15;			(Ce : La)	$AlCl_3$
$CeCl_3$–$PrCl_3$	1.16	1;	1.89	2	(Pr : Ce)	$AlCl_3$
$PrCl_3$–$NdCl_3$	1.13	3;	1.17	14	(Pr : Nd)	$AlCl_3$
La_2O_3–CeO_2	4.04	1;	5.27	2	(La : Ce)	$AlCl_3$
CeO_2–Pr_6O_{11}	33.5	2;	$\geqslant 100$	3	(Pr : Ce)	$AlCl_3$
Pr_6O_{11}–Nd_2O_3	1.63	1;	1.68	2	(Pr : Nd)	$AlCl_3$
Pr_6O_{11}–Nd_2O_3	1.30	5;	2.09	6	(Pr : Nd)	$AlCl_3$ and KCl

a) SF = Separation factor, b) FN = Fraction number.

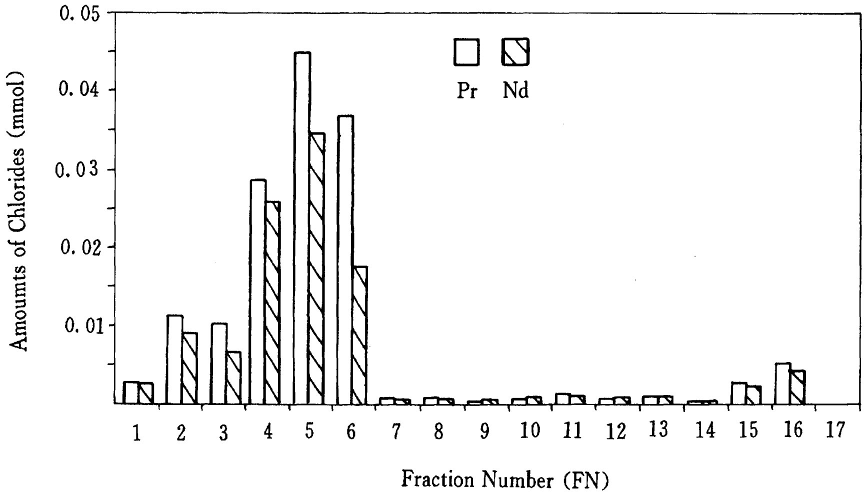

Fig. 4. Distribution of $PrCl_3$ and $NdCl_3$ deposits in a chemical vapor transport reaction formed from the binary oxide mixture Pr_6O_{11}–Nd_2O_3. The complex formers were $AlCl_3$ and KCl, and the atomic ratio in the raw material was C : K : Pr : Nd = 22 : 1 : 1 : 1.

ability order $LaCl_3 > CeCl_3 < PrCl_3 > NdCl_3$ in reactions 1, 2, and 3 (determined by their thermodynamic equilibrium constants at 1300 K) is benefit to the increase in the separation factor for La : Ce, Pr : Ce, and Pr : Nd from their oxide mixtures over from their chloride mixtures.

The exchange reactions,

$$(1/2)Ln_2O_3(s) + (3/4)Al_2Cl_6(g) = LnCl_3(l) + (3/2)AlOCl(s), \quad (6)$$

$$CeO_2(s) + Al_2Cl_6(g) = CeCl_3(l) + 2AlOCl(s) + (1/2)Cl_2(g), \quad (7)$$

$$(1/6)Pr_6O_{11}(s) + (11/12)Al_2Cl_6(g) = PrCl_3(l) + (11/6)AlOCl(s) + (1/3)Cl_2(g), \quad (8)$$

have been applied to the preparation of rare-earth chlorides from their oxides.[3,5—7,20—22] However, they would not be as important as the carbothermic reduction-chlorination reaction (Eqs. 1, 2, and 3) in this study, probably not only due to the high atomic ratio of C : Ln (7.5 : 1) in the raw materials and high flow rate of Cl_2 (15 cm^3 min^{-1}), but also due to the much larger standard Gibbs free-energy changes of reactions 1, 2, and 3 than of reactions 6, 7, and 8. This argument is supported by our preliminary separation experiments from Pr_6O_{11}–Nd_2O_3 without any Cl_2 in the carried gas (Fig. 5A) and from La_2O_3–CeO_2 without any active carbon in the raw material (Fig. 5B), in which cases the rare-earth chlorides would could be formed only by the exchange reactions (Eqs. 6, 7, and 8). The separation factors were only 1.19 for Pr : Nd in the former case and 5.47 for La : Ce in the latter case. On the other hand, the transport of the vapor complexes would also be important for whole reaction. Figure 5C shows another preliminary separation experiment from La_2O_3–CeO_2, where active carbon was both mixed in the raw material and fully added into all of the receptors, resulting in a poor transport condition. The separation factor was only 5.72 for La : Ce.

Furthermore, as a combination of several multi-phase reactions carried out continuously in a flow system, the distribution profiles of its resulting chlorides in the transported deposits may be affected by many thermodynamic and kinetic factors, as shown in Figs. 2, 3, 4, and 5. Although the values of 1.84—2.09 for the separation factor for Pr : Nd from Pr_6O_{11}–Nd_2O_3 obtained in the this study would be the largest, or nearly the largest, ones that have been reported for the neighboring element pair, they are still much smaller than 21.4 for La : Ce and $\geqslant$100 for Pr : Ce, as listed in Table 1. Therefore, a further study of further increasing the separation factor between Pr and Nd is in progress.

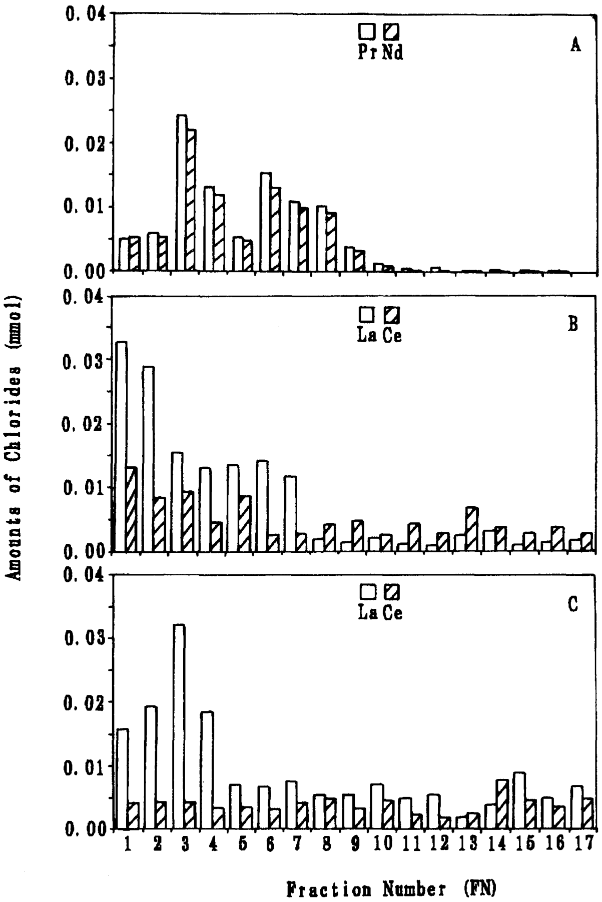

Fig. 5. Distribution of $PrCl_3$ and $NdCl_3$ or $LaCl_3$ and $CeCl_3$ deposits in a chemical vapor transport reaction formed from the binary rare earth oxide mixtures at special conditions: (A) Pr_6O_{11}–Nd_2O_3 but without Cl_2 in the carried gas, (B) La_2O_3–CeO_2 but without active carbon in the raw material, and (C) La_2O_3–CeO_2 where active carbon was not only mixed in the raw material but also fully added into each of the receptors. The complex former was $AlCl_3$ and the atomic ratio in the raw material was C : Ln : Ln′=15 : 1 : 1.

Conclusions

This paper presents the first experimental evidence that the mutual separation between the neighboring rare-earth elements La, Ce, Pr, and Nd can be realized within 6 h, not only from their binary chloride mixtures, but also from their binary oxide mixtures using a chemical vapor-transport process, in which the separation efficiency is much higher from the oxide mixtures than from the chloride mixtures under a definite reaction condition, and that addition of KCl into the raw material of the oxide mixture Pr_6O_{11}–Nd_2O_3 can further increase the separation factor for Pr : Nd. The separation factors of 21.4 for La : Ce, $\geqslant$100 for Pr : Ce, and 1.84— 2.09 for Pr : Nd from their binary oxide mixtures obtained in this study would be the largest, or nearly the largest, ones that have been reported for the three neighboring element pairs. These results indicate the great potential industrial applicability of the dry process for the oxide mixtures than for the chloride mixtures. This dry process should also be useful for a mutual separation between other pairs of neighboring rare-earth elements from their oxide mixtures.

This work was supported by the Doctorial Foundation of the State Educational Committee and the National Science Foundation of China. The publication of this paper is partly sponsored by the Wang Zhao-Fan Commemoration Fund of NEU.

References

1) H. A. Oye and D. M. Gruen, *J. Am. Chem. Soc.*, **91**, 2229 (1969).
2) M. Cosandey and F. P. Emmenegger, *J. Electrochem. Soc.*, **126**, 1601 (1979).
3) G. N. Papatheodorou and G. H. Kucera, *Inorg. Chem.*, **18**, 386 (1979).
4) H. Schafer and U. Florke, *Z. Anorg. Allg. Chem.*, **479**, 89 (1981).
5) G. Steidl, K. Bachmann, and F. Dienstbach, *J. Phys. Chem.*, **87**, 5010 (1983).
6) G. Steidl, F. Dienstbach, and K. Bachmann, *Polyhedron*, **2**, 727 (1983).
7) Z. -C. Wang, L. -S. Wang, R. -J. Gao, and Y. Su, "Thermodynamic Study of the Rare Earth Vapour Complexes: $ScAl_2Cl_9$ and YAl_2Cl_9," *J. Chem. Soc., Faraday Trans.*, in press.
8) G. I. Novikov and A. K. Baev, *Zh. Neorg. Khim.*, **9**, 1669 (1964).
9) G. I. Novikov and F. G. Gavryuchenkov, *Zh. Neorg. Khim.*, **10**, 2706 (1965).
10) F. G. Gavryuchenkov and G. I. Novikov, *Zh. Neorg. Khim.*, **11**, 1515 (1966).
11) F. G. Gavryuchenkov and G. I. Novikov, *Vestn. Leningr. Univ.*, **4**, 106 (1966).
12) G. Adachi, S. Shinozaki, Y. Hirashima, and K. Machida, *J. Less-Common Met.*, **169**, L1 (1991).
13) G. Adachi, K. Murase, S. Shinozaki, and K. Machida, *Chem. Lett.*, **1992**, 511.
14) K. Murase, S. Shinozaki, K. Machida, and G. Adachi, *Bull. Chem. Soc. Jpn.*, **65**, 2724 (1992).
15) K. Murase, S. Shinozaki, Y. Hirashima, K. Machida, and G. Adachi, *J. Alloys Comp.*, **198**, 31 (1993).
16) K. Murase, K. Machida, and G. Adachi, *Chem. Lett.*, **1994**, 1297.
17) K. Murase, K. Machida, and G. Adachi, *Chem. Lett.*, **1992**, 1555.
18) K. Murase, K. Machida, and G. Adachi, *J. Alloys Comp.*, **217**, 218 (1995).
19) R. K. Winge, V. J. Peterson, and V. A. Fassel, *Appl. Spectrosc.*, **33**, 206 (1979).
20) H. Gunsilius, W. Urland, and R. Kremer, *Z. Anorg. Allg. Chem.*, **550**, 35 (1987).
21) D. Hake and W. Urland, *Angew. Chem.*, **101**, 1416 (1989).
22) D. Hake and W. Urland, *Z. Anorg. Allg. Chem.*, **586**, 99 (1990).