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A novel process of extraction and separation of RE and Mn from Panxi rare earth mud^①

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[Abstract] A novel process to extract and separate rare earth (RE) and manganese (Mn) from Panxi rare earth mud was developed. The process involves roasting the mud at 480 °C with NH₄Cl as chlorinating agent, and leaching the calcine with hot water to obtain a rare earth chloride solution. After the solution was further purified, HD(DIBM)P (P₅₀₇) was applied as extractant to separate RE and Mn. By seven stages of fractional extraction, the RECl₃ and MnCl₂ solutions with 99.8% purity were obtained. Finally, the purified RECl₃ and MnCl₂ solution were precipitated by NH₄HCO₃ to obtain a crystal RE₂(CO₃)₃ and MnCO₃ products respectively.

[Key words] rare earth mud; extraction and separation; Mn and RE

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1 INTRODUCTION

Panxi rare earths (RE) deposit is the second largest rare earth deposit in China. Geological study showed that the deposit has severely weathered, and about 20% RE are in the form of black weathered mud. The RE mud weathered contains 3% ~ 7% RE oxides and 2% ~ 10% Mn oxides in enriched form, and be referred to as weathered RE mud (WREM). The RE content at this level in the WREM is of economic value and worth recovering. However, the RE in the WREM co-existed as a colloidal sediment phase disseminate in amorphous manganese/iron oxides^[1~4]. The conventional physical processing methods, as flotation, magnetic, gravity and electronic separation, were found ineffective to recover RE from such WREM. The recent studies showed a promise for RE and Mn recovery from the WREM based on roasting with NH₄Cl to chlorinate RE and Mn^[5,6].

The study also found that the manganese in the WREM of Panxi RE deposit mainly exists as MnO₂, MnO(OH) and Mn₂O₃. These manganese oxides are highly soluble and dissolve readily during chemical leaching, releasing manganese along with RE elements in leachates. At the same time, most manganese could also be leached by roasting WREM with NH₄Cl^[5,6].

To maximize the utility of natural resources, manganese should be considered as an integral part of the process. Based on the studies of the mineralogical

properties of the WREM, the process involving roasting of the mud mixed with NH₄Cl followed by direct water leaching was developed. About 80% RE and 70% Mn could be leached, however, about 30% RE would be lost when the impurity Mn²⁺ was removed from leaching solution by oxidizing Mn²⁺ to MnO₂^[5,6]. Separating Mn is also an important problem for recovering RE from the WREM. Here HD(DIBM)P (P₅₀₇) is chosen as an extractant to separate RE and Mn in the leaching solution. RECl₃ and MnCl₂ are further respectively precipitated by NH₄HCO₃ to obtain RE₂(CO₃)₃ and MnCO₃ product. Therefore the destination of this study is to develop a new process to recover RE and Mn from Panxi WREM which has not been utilized in industry.

2 EXPERIMENTAL

2.1 Materials

The WREM sample was obtained from Panxi rare earth deposit. The mineralogical study showed that amorphous manganese oxides and crystalline aluminum oxide and silica were the major phases. Manganese was distributed among MnO₂, MnO(OH) or Mn₂O₃^[3,4]. The major chemical components of the sample are shown in Table 1.

The RE existing state of the sample was determined by the phase analysis investigation^[1,3]. The RE in the WREM was divided into water dissoluble phase, ion phase, colloid sediment phase and mineral

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Table 1 Major chemical components of Panxi WREM (%)

RE	Mn	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	K ₂ O
5.88	1.86	37.97	9.40	6.10	0.77	4.13

phase. Results illustrate that about 80% RE is disseminated in the colloid sediment phase, and less than 3% RE exists as the water dissoluble phase and ion phase. Actually the colloid sediment phase is the aggregate of rare earth elements combined with iron and manganese by oxide bonds. Therefore the RE in the WREM is commonly considered as the RE oxide.

2.2 Experimental procedures and analytic methods

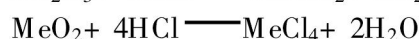
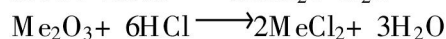
The chlorinating RE experiments were carried out by mixing NH₄Cl with the WREM sample and roasting in muffle furnace. The calcine was directly leached by 60~90 °C hot water. To remove Pb from leaching solution, a little sulfate was added into the leaching system before filtering. By filtering and cooling, the leaching solution can be used to recover RE and Mn.

All extraction experiments were carried out at 25 °C, by adding 60 mL HD(DIBM) (P₅₀₇) organic phase and 60 ml water phase into separating funnel, mixing 5 min at Kahn agitator. After stewing and delamination of the extraction system, the RE content of separated solution was analyzed by EDTA, titration and Mn contents were analyzed by sodium arsenite-sodium nitrite titration^[7].

3 RESULTS AND DISCUSSION

3.1 Chlorinating RE of mud by NH₄Cl roasting

The chlorinating agent was the decomposed HCl from thermal decomposition of NH₄Cl for the studied system. The roasting reactions can be collectively represented as^[2,7]:



Most metals (Me), such as Ca, Mn, Ba and RE, were converted to metal chlorides, depending on the reaction conditions. The roasting reactions were carried out under the temperature below 500 °C so that the conversion of unwanted metals was kept at minimum while maximizing the RE conversion^[5]. In this context, the roasting temperature is the key parameter. The amount of chlorinated RE of Panxi WREM sample vs roasting temperature is shown in Fig. 1. As the roasting temperature is higher than 480 °C, the amount of chlorinated RE is decreased. It could be explained by the further decomposition reaction of RECl₃ as^[8]

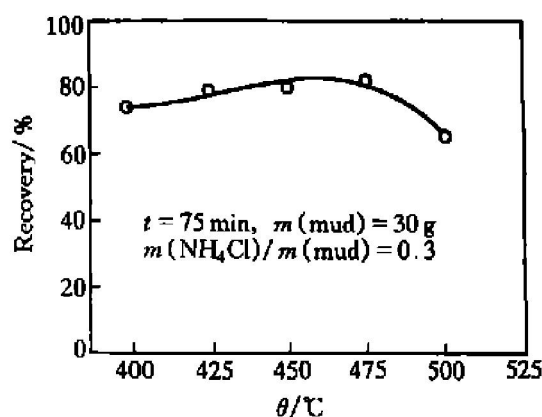
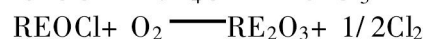
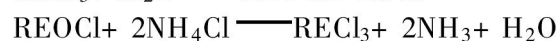


Fig. 1 Effect of roasting temperature on RE chlorinating

This phenomenon is also in accordance with the described observation of preparing anhydrous RE-Cl₃^[7]. Therefore the suitable roasting temperature should be 480 °C for effective chlorinating RE of the WREM with NH₄Cl.

Effect of roasting time on RE chlorinating at 450 °C and 480 °C is shown in Fig. 2, which illustrates that the RE recovery increases with increasing roasting time when the roasting time is less than 75 min. The RE recovery decreases when roasting time is longer than 75 min. It may also be caused by decomposition of RECl₃ for the longer roasting time as the observation at high temperature.

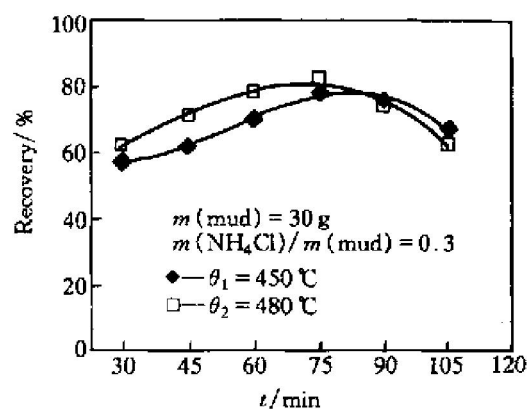


Fig. 2 Effect of roasting time on RE chlorinating

Effect of NH₄Cl dosage on RE chlorinating at a given roasting temperature is shown in Fig. 3. The RE recovery increases with increasing addition of NH₄Cl. As NH₄Cl amount reaches $m(\text{NH}_4\text{Cl})/m(\text{mud}) = 0.3$, no obvious increase of RE recovery could be observed at larger $m(\text{NH}_4\text{Cl})/m(\text{mud})$. So $m(\text{NH}_4\text{Cl})/m(\text{mud}) = 0.3$ is the suitable ratio for the system.

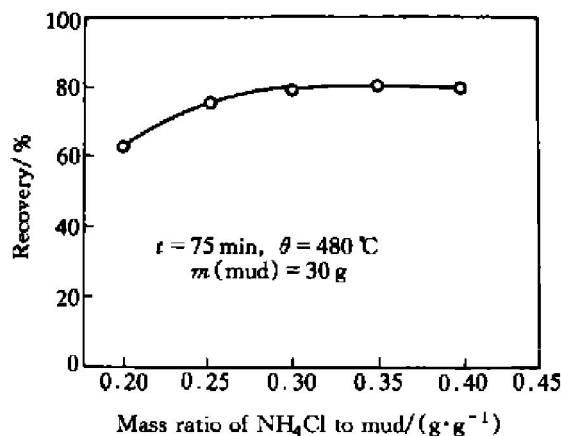


Fig. 3 Effect of NH_4Cl dosage on RE chlorinating

3.2 Separation of RE and Mn from leaching solution

The WREM sample was roasted with NH_4Cl at optimum condition. The calcine was leached by hot water ($90\text{ }^\circ\text{C}$) and filtrated. A leaching solution contained RE was obtained, and its composition is listed in Table 2. The results illustrates that major impurities in the leaching solution are Mn^{2+} and NH_4^+ . To obtain the pure RE and Mn product, it is necessary to separate Mn from the contained RE solution first.

Table 2 Major chemical composition of RE leaching solution ($\text{mol}\cdot\text{L}^{-1}$, $\text{pH}=4.0$)

RE^{3+}	Mn^{2+}	NH_4^+	Fe
0.1045	0.7075	1.348	3.25×10^{-6}

Generally speaking, extraction is an effective method to separate impurities of solution system. But it should be selected a suitable extractant for the real solution. In this context, the major impurity to be purified is the manganese. By comparing the properties of different extractants, 20% HD (DIBM) P (P_{507}) kerosene extractant is chosen to purify the studied leaching solution^[9].

3.2.1 Single stage experiment

The relationship of RE and Mn extracting ratio with equilibrium pH in water phase is shown in Fig. 4. The results show that RE and Mn in the leaching solution can be easily separated at $\text{pH} 0\sim 3$, RE extracting ratio reaches above 90% at $\text{pH}=3$. The extracting sequence is: $\text{RE}^{3+} > \text{Mn}^{2+}$. Therefore the HD(DIBM) P (P_{507}) is the effective extractant to separate RE and Mn.

The relationship between RE/Mn separating coefficient and equilibrium pH in water phase is shown in Fig. 5. It further illustrates that RE/Mn coefficient is larger than 20 at $\text{pH} 0\sim 3$, so it can easily separate RE and Mn with HD(DIBM) P (P_{507}) as a extractant for the studied system.

3.2.2 Multi-stage to separate RE/Mn

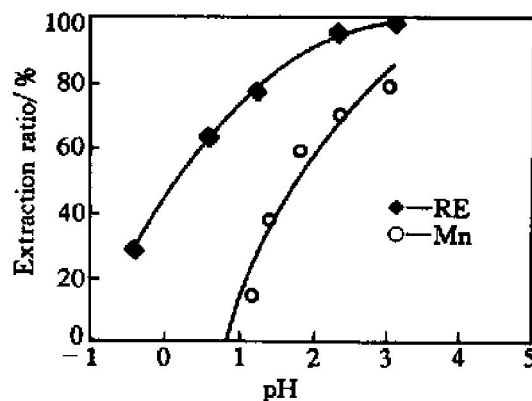


Fig. 4 Extraction efficiency of metals as function of equilibrium pH

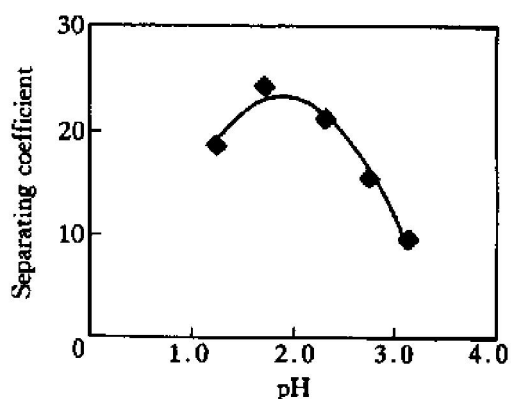


Fig. 5 Separating coefficient of RE/Mn vs equilibrium pH for leaching solution

The multistage scheme to separate RE/Mn with HD(DIBM) P (P_{507}) is shown in Fig. 6.

Based on the calculation of multi-stage extraction^[2], leaching solution is extracted by a multi-stage system. As the system reaches equilibrium, the analysis results of the raffinate sample are listed in Table 3. The results show that Mn purity is higher than 99.5%, and its recovery is higher than 98.8%.

The stripping liquid analysis results of organic phase outlet are also listed in Table 4. The purity of RE is above 99.5%, and its recovery is higher than 99%. The results can be further plotted as Fig. 7. It can be further illustrated that the Mn purity is greater than 99% with 3 stages extraction. Therefore extraction with 7 stages is enough to separate RE and Mn.

3.3 Preparation of MnCO_3 and $\text{RE}_2(\text{CO}_3)_3$

3.3.1 Preparation of MnCO_3

The MnCl_2 solution from raffinate liquid is precipitated by 20% NH_4HCO_3 solution. Filtering, washing and drying 2 h at $100\text{ }^\circ\text{C}$, a MnCO_3 product is obtained, the Mn content is 44.03%, which is in accordance with the Chinese national standard GB10503-89 (44.0% ~ 46.0%) for MnCO_3 product.

3.3.2 Preparation of crystal $\text{RE}_2(\text{CO}_3)_3$ product

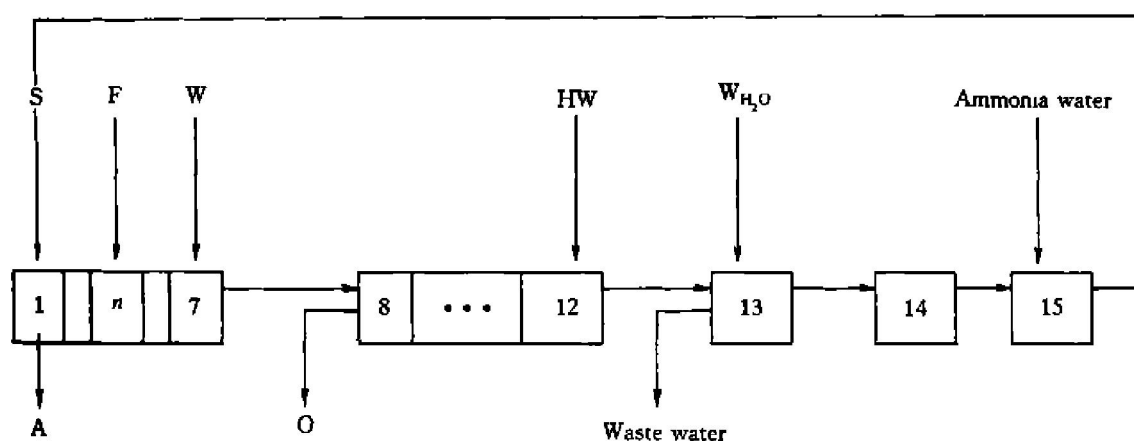


Fig. 6 Simplified scheme of multistage extraction separation
(S: P₅₀₇ organic phase; F: Leaching solution; W: Washing acid; HW: stripping acid;
W_{H₂O}: washing water; A: Faffinate; O: stripping liquid)

Table 3 Analysis results of faffinate

No.	Mn Concentration/ (g·L ⁻¹)	RE Concentration/ (g·L ⁻¹)	Mn purity/ %	Mn recovery/ %	Water phase pH
A-11	18.68	0.0733	99.61	99.10	4.0
A-12	18.92	0.0772	99.59	100.00	4.0
A-13	18.68	0.0719	99.62	99.10	4.0
A-14	18.30	0.0668	99.64	97.08	4.0
A-15	18.30	0.0617	99.66	97.08	4.0

Table 4 Stripping liquid analysis results of organic phase outlet

No.	RE Concentration/ (g·L ⁻¹)	Mn Concentration/ (g·L ⁻¹)	RE purity/ (%)	RE recovery/ %
O-11	22.61	0.0583	99.74	103.2
O-12	22.91	0.0200	99.13	104.6
O-13	21.15	0	100	96.58
O-14	21.15	0	100	96.58
O-15	20.67	0	100	94.37

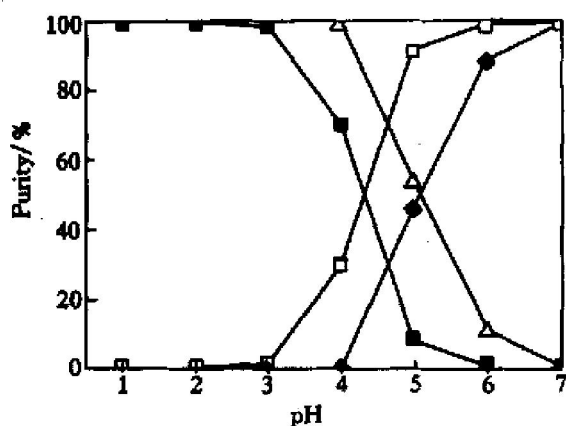


Fig. 7 RE and Mn purity in each stage

- ▲ — RE phase in water phase;
- — RE purity in organic phase;
- △ — Mn purity in water phase;
- ◆ — Mn purity in organic phase

Stripping the HD (DIBM) P (P₅₀₇) organic phase, a RECl₃ solution with purity of 99.5% is obtained. The RECl₃ solution is further precipitated by 20% NH₄HCO₃ solution. Chemical analysis determined its water-containing amount, the results are shown in Table 5. The product of RE₂(CO₃)₃ contains 7 crystal water molecules, it can be represent as RE₂(CO₃)₃ · 7H₂O. SEM determined the product possesses the morphology as shown in Fig. 8.

4 CONCLUSION

A novel process to extract and separate rare earth (RE) and manganese (Mn) from Panxi rare earth mud (WREM) was developed. The process involves the roasting of mud at 480 °C with NH₄Cl as chlorinating agent, leaching of calcine with hot water to obtain a rare earth chloride solution. The HD (DIBM) P (P₅₀₇) is used to separate RE and Mn, the

Table 5 Comparing between theoretical calculation and experimental analysis (%)

Product	Theoretical value			Experimental results			RE purity/ %
	REO	CO ₂	H ₂ O	REO	CO ₂	H ₂ O	
RE ₂ (CO ₃) ₃ •7H ₂ O	56.51	30.34	21.24	55.21	31.06	21.74	97.7

**Fig. 8** SEM morphology of RE₂(CO₃)₃•7H₂O

RECl₃ and MnCl₂ solutions with purity over 99% can be obtained respectively. Their recoveries are higher than 98%. Furthermore the purified RECl₃ and MnCl₂ solutions are precipitated by NH₄HCO₃, a MnCO₃ product and a crystal RE₂(CO₃)₃ product are obtained respectively.

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