

DEVELOPMENT OF AN INNOVATIVE MIXED CHLORIDE LEACHING PROCESS FOR THE RECOVERY OF RARE EARTHS

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ABSTRACT

Rare earth elements and yttrium (REEs+Y) are being used in the making of hybrid electric cars, catalytic converters, wind power generators, LEDs, hard disc drives, flat panel displays, and portable electronics. Currently China produces more than 95% of REEs+Y, which has made REEs+Y a critical strategic resource. Process Research ORTECH Inc. (PRO) has developed the innovative mixed-chloride (HCl+MgCl₂) solvent extraction processes for recovery of REEs+Y from their ores. The HCl leaching system provides the opportunity to regenerate the acid, while the presence of MgCl₂ in the lixiviant enhances the activity of the hydrogen ion by orders of magnitude, making the lixiviant very aggressive and resulting in high recoveries of REEs+Y. Solvent extraction steps are used for separation and purification of REEs+Y from other value metals or impurities including iron, zirconium, hafnium, uranium, thorium, niobium, tantalum and titanium. Direct individual separation of REEs+Y in a mixed chloride system allows avoiding the additional process steps of precipitation and dissolution in HCl. The resulting process has a simplified flow sheet that is closed-loop and environmentally friendly.

KEYWORDS

Rare earth elements, mixed chloride leaching, solvent extraction, rare earth separation

INTRODUCTION

Rare earth elements (REEs) include 15 elements from the lanthanide series plus yttrium, and occasionally scandium. REEs are further subdivided in two groups: light rare earth elements (LREEs) and heavy rare earth elements (HREEs). LREEs include elements from lanthanum (La) to europium (Eu), while HREEs include elements from gadolinium (Gd) to lutetium (Lu) plus yttrium. The REEs are not as rare as implied by their name. Cerium is more abundant than tin, yttrium is more abundant than lead, and all of the lanthanides are more plentiful than platinum group metals. REEs have numerous applications, including strength permanent magnets, catalysts, liquid crystal displays, glass additives, magnetic materials, lasers, ophthalmic lenses, and alloying elements for hardening.

Although REEs are not rare and the rare earth oxides are scattered around the globe, over 95% of REEs+Y are currently produced in China (Pitts, 2011). On one hand the Chinese government is restricting the export of REEs, and on the other hand the demand for REEs+Y is increasing in the rest of the world. This has created an imbalance in the supply and demand of REEs, and has led to a rush in the development of new REE projects.

Generally, the process for the production of REEs+Y starts with crushing and grinding of ore, followed by concentration (Rare Earth Ore Processing, 2013). The concentrate then undergoes roasting or cracking to make REEs+Y and zirconium amenable to leaching. The calcine undergoes leaching to bring zirconium and REEs+Y into solution, followed by solid/liquid separation. The solid tailing undergoes stabilization before disposal. The pregnant leach solution (PLS) undergoes purification to remove impurities, so that these impurities do not show up in the final product. After purification, REEs are precipitated from the PLS by addition of oxalic acid. If rare earth oxalates are precipitated from the PLS, the rare earth oxalates are subsequently calcined and re-dissolved in hydrochloric acid, and then individual REEs+Y are separated using solvent extraction. However, this is highly complicated and costly as acid/caustic used in roasting and cracking is not recycled.

PRO CHLORIDE PROCESS FOR RARE EARTH ELEMENT SEPARATION

Process Research Ortech Inc. (PRO) has developed an innovative process for the production of rare earths that is much simpler, cost effective and environmentally friendly (Lakshmanan et al., 2013). The PRO process uses a leach in a mixed chloride lixiviant that has been found to be very effective in the processing of a number of ores. Chloride chemistry is complex and quite different from corresponding sulphate systems. The solubility of metal chlorides is generally higher than their corresponding sulphate salts. For example, the solubility of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is about one fifth that of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, while nickel and ferrous chlorides are also more soluble than their sulphate counterparts. This allows the use of more concentrated solutions (Lakshmanan et al., 2004). Also, the activity of water is $\ll 1$ in concentrated magnesium chloride salt solutions, and the activity of the hydrogen ion, H^+ (or H_3O^+) increases rapidly with chloride concentration as shown in Figure 1 (Jansz, 1983). This enhances the leachability of minerals in mixed chloride solutions, resulting in increased metals recovery. PRO has been at the forefront of technological development of chloride metallurgy, and PRO's patented mixed chloride technology has been applied to the recovery of several products, including titanium dioxide from ilmenite ores, REEs+Y from alumino-silicate ores, base metals and PGMs from sulfide ores, gold from refractory ores, and base metals from laterite ores (Bell et al., 1977; Christies et al., 1974; Harris et al., 2004, 2006, 2007, 2010; Lakshmanan et al., 1974, 2008, 2011, 2012, 2013).

Mixed Chloride Leaching

Based on PRO's proprietary mixed chloride leaching technology (Lakshmanan et al., 2013), a rare earths-containing ore was subjected to grinding, followed by leaching with a lixiviant of hydrochloric acid and magnesium chloride at 95°C for 4h in a 1L glass reactor with vapor condensing system. The leach slurry was subjected to solid/liquid separation. The ore sample and the solid residue were digested and analyzed by inductively coupled plasma (ICP) spectrometry. The elemental concentrations in the pregnant

leach solution (PLS) were also determined with ICP analysis. Results are shown in Table 1. Extractions of REEs and REEs+Y were 86.1% and 83.3%, respectively.

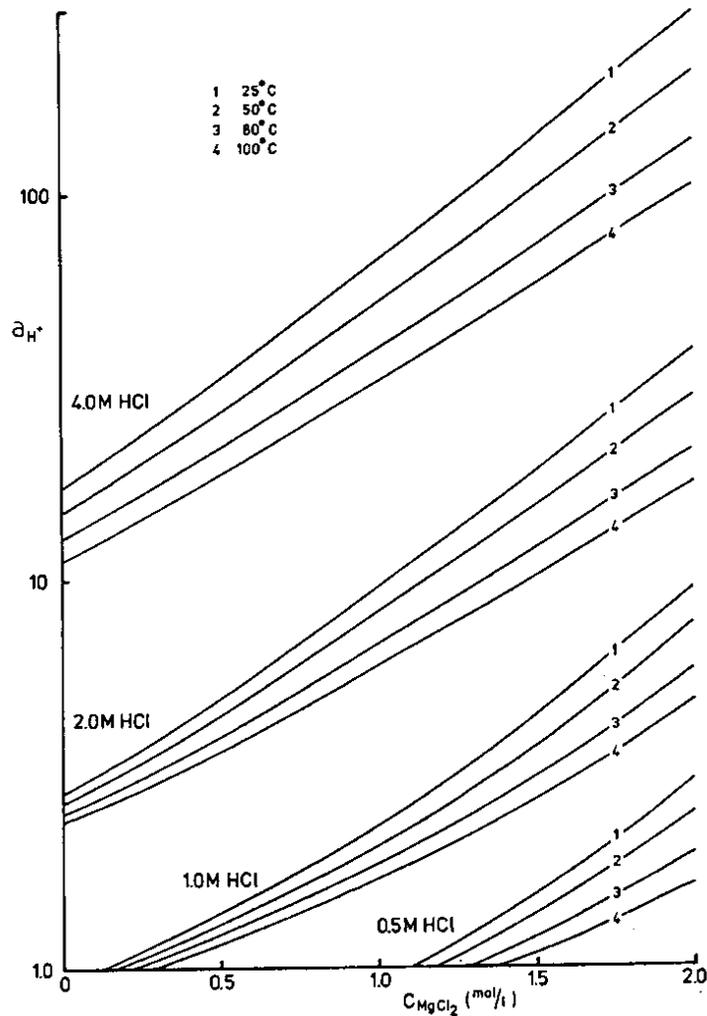


Figure 1 - Effect of $MgCl_2$ concentration on the activity of H^+ in HCl solutions (Jansz, 1983)

Table 1 - Results on extraction of REEs and REEs+Y by PROs proprietary mixed chloride leaching technology (Lakshmanan et al., 2013)

100 mesh	HCl	$MgCl_2$	Solids	Temp	Time	REEs	REEs+Y
%	(N)	(mg/L)	(w/w)	$^{\circ}C$	(hr)	(%)	(%)
85	5.8	225	10.4	95	4	86.1	83.3

Solvent Extraction for Zirconium and Acid Recovery

The PLS undergoes multiple stage solvent extraction to remove Fe and other impurities, including U, Th, Cu, and Zn, followed by the recovery of zirconium. More than 99% Fe was extracted with 20% ketone extractant and 20% EXXAL 13 in kerosene from the PLS. Impurities were extracted from the Fe raffinate with a tertiary amine (Alamine 336) in kerosene. The results are shown in Table 2. This raffinate was subjected to solvent extraction of Zr with 20% 2-ethylhexyl phosphonic acid mono-2-ethylhexylester (PC-88A) and 20% Shellsol EXXAL™ 13 in kerosene. Extraction was carried out for 5 minutes at room temperature at an organic/aqueous ratio of 1. More than 99% Zr was selectively extracted over rare earths under these conditions (Table 2). The Zr raffinate was treated for extraction of free hydrochloric acid using EXXAL™ 10 at room temperature at an organic/aqueous ratio of 1. The concentration of free HCl was decreased from 3.1 N to 0.8 N under these conditions. The pH of acid-extracted Zr raffinate was 1.5. The extracted free acid can be recycled to the leaching stage.

Table 2 - Results on separation of multiple elements including Zr from pregnant leach solution by multi-stage solvent extraction process

	Fe	Zr	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
Concentration (mg/L)										
Pregnant Leach	7940	2490	638	1290	168	555	148	7	152	25
Iron raffinate	0.6	2440	626	1260	173	607	145	7	150	25
Impurities raffinate	0.6	2330	668	1340	168	591	140	7	151	27
Zirconium raffinate	0.5	5	768	1550	174	612	146	8	152	30
	Dy	Ho	Er	Tm	Yb	Lu	Y	Cu	Zn	U
Concentration (mg/L)										
Pregnant Leach	176	31	90	12	67	8	746	125	111	14
Iron raffinate	171	34	98	13	70	8	788	127	116	13
Impurities raffinate	176	35	101	14	73	9	744	4	2	0
Zirconium raffinate	208	41	115	15	71	8	772	1	2	<0.05
	Hf	Al	Ca	K	Mg	Mn	Na	S	Si	Sr
Concentration (mg/L)										
Pregnant Leach	74	1180	8570	854	54159	267	1580	113	12	120
Iron raffinate	72	1280	9250	973	54677	299	1710	129	16	125
Impurities raffinate	72	1120	8120	859	54780	187	1490	114	8	135
Zirconium raffinate	1	1170	8750	915	58685	172	1590	123	9	125

Rare Earths Recovery

REEs+Y were precipitated from acid-extracted Zr raffinate with 10% oxalic acid at pH 2.0. Around 99% of the REEs+Y was precipitated at room temperature. Results are shown in Table 3. The rare earth oxalate obtained was washed with water, dried, and dissolved in hydrochloric acid to give a REEs+Y concentrate for individual separation by solvent extraction. Alternatively, D2EHPA with EXXAL™ 13 in kerosene was used for direct extraction of REEs+Y from acid-extracted Zr raffinate (Table 4). Pregnant strip of REEs+Y can undergo solvent extraction for individual separation. The raffinate from the final solvent extraction stage is recycled to the leaching stage as shown in Figure 2.

Table 3 - Results on REEs+Y precipitation from Zr raffinate with 10% oxalic acid

	Fe	Zr	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
	Concentration (mg/L)									
Zirconium raffinate	0.5	5	768	1550	174	612	146	8	152	30
REEs+Y precipitate filtrate	0.5	<0.5	46.2	32.0	2.4	6.6	1.2	0.1	1.5	0.3
REEs+Y precipitation (%)			94	98	99	99	99	99	99	99
	Dy	Ho	Er	Tm	Yb	Lu	Y	Cu	Zn	U
	Concentration (mg/L)									
Zirconium raffinate	208	41	115	15	71	8	772	1	2	<0.05
REEs+Y precipitate filtrate	1.2	0.3	0.7	0.1	0.1	0.5	10	1	4	<0.05
REEs+Y precipitation (%)	99	99	99	99	100	94	99			
	Hf	Al	Ca	K	Mg	Mn	Na	S	Si	Sr
	Concentration (mg/L)									
Zirconium raffinate	1	1170	8750	915	58685	172	1590	123	9	125
REEs+Y precipitate filtrate	<0.02	1710	7860	1324	66728	160	2140	121	17	155

Table 4 - Results on REEs+Y extraction from acid-extracted Zr raffinate

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm
	Concentration (mg/L)											
Acid-extracted Zr Raffinate	50	70	6	54	13	<5	19	7	28	7	19	<5
REEs+Y Raffinate	<5	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
	Yb	Lu	Y	Zr	Fe	Ti	Al	Ca	Cu	K	Na	Zn
	Concentration (mg/L)											
Acid-extracted Zr Raffinate	16	5	184	<5	<5	<5	7182	5712	<5	1611	4397	<5
REEs+Y Raffinate	<5	<5	<5	<5	<5	<5	6683	5628	<5	1468	4411	<5

CONCLUSIONS

REEs+Y ores are typically processed by acid/caustic baking, followed by leaching, solvent extraction, precipitation of REEs+Y, re-dissolution of the rare earth precipitate in hydrochloric acid, and recovery of individual REEs by solvent extraction. PRO has developed an innovative process for the production of REEs+Y using a mixed chloride leach process. The PRO process includes leaching in mixed chlorides, followed by multiple-stage solvent extraction to remove Fe and other impurities, including U, Th, Cu, and Zn, followed by the recovery of Zr. Zr recovery reached more than 99%. Free hydrochloric acid was selectively recovered from Zr raffinate and recycled back to leaching stage. Around 99% of REEs+Y was precipitated from acid-extracted Zr raffinate with 10% oxalic acid. Alternatively, REEs+Y were directly extracted from acid-extracted Zr raffinate. The REEs+Y pregnant strip solution can undergo processes for separation of individual REEs+Y. REEs+Y raffinate is recycled to the leaching stage. The process flowsheet developed by PRO is efficient and environmentally friendly.

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