

**AN INTEGRATED PROCESS FOR SEPARATION AND PURIFICATION OF RARE EARTH ELEMENTS IN CHLORIDE MEDIUM**

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**ABSTRACT**

This paper describes development of an integrated chloride process for separation and purification of REEs. The process includes atmospheric leaching of ore/concentrate with mixed chloride lixiviant containing HCl and MgCl<sub>2</sub> followed by bulk recovery of REEs, dissolution of the bulk intermediate product, and separation of individual REEs by solvent extraction (SX) process steps. Mixed chloride leaching technology provides the opportunity to regenerate the lixiviant, while the addition of MgCl<sub>2</sub> in HCl enhances the hydrogen ion activity by orders of magnitude increasing REE extraction efficiency at a lower concentration of HCl. An individual REE separation process developed by Innovation Metals Corp. is being piloted at a state-of-the-art facility at Process Research ORTECH Inc. in Mississauga, Ontario, Canada. The SX process includes the separation of light REEs (La – Nd), medium REEs (Sm – Gd) and heavy REEs (Tb – Lu plus Y) from leach liquor followed by individual REE separation. Each SX circuit proceeds by multistage extraction followed by scrubbing and stripping. The process is chloride based and reagents are recycled, reducing waste generation and optimizing water usage to reduce environmental impact.

**KEYWORDS**

Rare earth elements, Chloride leaching process, Solvent extraction, REEs separation

## INTRODUCTION

Rare earth elements (La to Lu plus Y) exhibit a range of unique magnetic, electronic, catalytic and optical properties. Due to these special properties, the application of REEs is increasing and they are found in components for wind power generation, hybrid electric cars, catalytic converters, and many electronic devices.

Rare earth elements (REEs) are commonly divided in two groups: light rare earth elements (LREEs) and heavy rare earth elements (HREEs). Light rare earth elements include elements from lanthanum (La) to neodymium (Nd). Although promethium (Pm) is considered an LREE it is unstable and scarcely occurs in nature and is generally excluded. Heavy rare earth elements include elements from samarium (Sm) to lutetium (Lu) plus yttrium. Although rare earth elements 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 rare earth elements 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 rare earth elements and has led to a rush for developing new rare earth projects.

### PRO CHLORIDE PROCESS FOR RARE EARTH ELEMENTS SEPARATION

Process Research ORTECH Inc. (PRO) has developed an innovative process for the production of rare earths that is cost effective and environmentally friendly (Lakshmanan et al., 2015). The PRO process uses a mixed chloride leach 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 sulfate 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 enables 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,  $\text{H}^+$  (or  $\text{H}_3\text{O}^+$ ) increases rapidly with chloride concentration as shown in Figure 1 (Jansz, 1983). This helps to enhance the leachability of minerals in mixed chloride solutions resulting in potentially increased metals recovery. PRO has been developing technology for chloride metallurgy. PRO's patented mixed chloride technology has been applied for the recovery of metals and compounds including titanium dioxide from ilmenite ores, nickel and cobalt from lateritic ores, REEs+Y from alumino-silicate ores, base metals and PGM from sulfide ores, and gold from refractory ores (Bell et al., 1977; Christies et al., 1974; Harris et al., 2004, 2006, 2007, 2010; Lakshmanan et al., 1974, 2008, 2011, 2012, 2015).

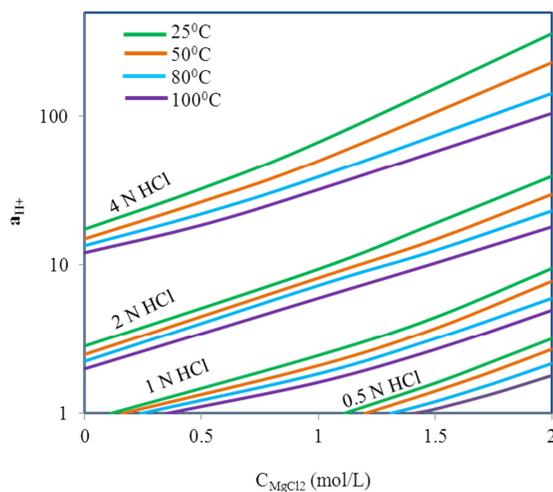


Figure 1 – Effect of  $\text{MgCl}_2$  concentration on the activity of  $\text{H}^+$  in HCl solutions (Jansz, 1983)

### Mixed Chloride Leaching

Based on PRO's proprietary mixed chloride leaching technology (Lakshmanan et al., 2015), 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 4 hours. 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). The elemental concentrations in the pregnant leach solution (PLS) were also determined by ICP. Leaching conditions and recovery of rare earth elements are shown in Table 1. Extractions of REEs and REEs plus yttrium (REEs+Y) were 86.1% and 83.3%, respectively. A conceptual flowsheet is presented in Figure 2.

Table 1 – Results on extraction of rare earth elements plus yttrium (REEs+Y) by PRO's proprietary mixed chloride leaching technology (Lakshmanan et al., 2015)

100 mesh (%)	HCl (N)	MgCl <sub>2</sub> (g/L)	Solids (% w/w)	Temp (°C)	Time (h)	REEs (%)	REEs+Y (%)
85	5.8	225	10.4	95	4	86.1	83.3

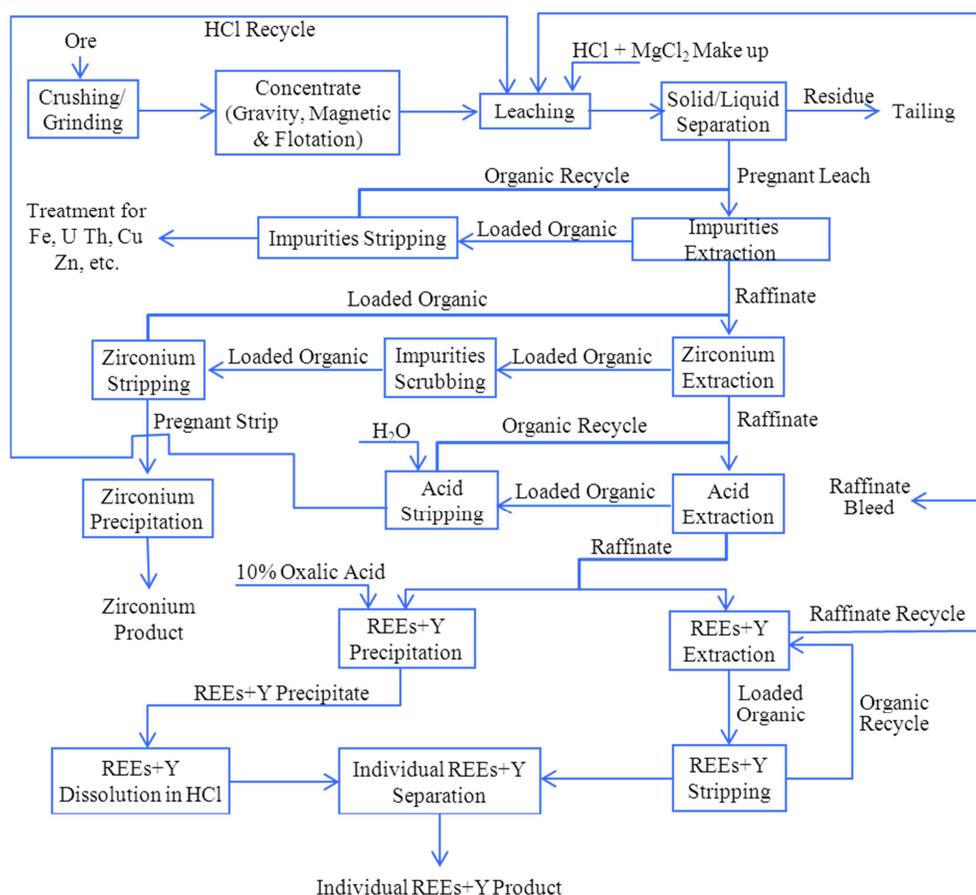


Figure 2 – Flowsheet for REEs+Y recovery by PRO's mixed chloride leaching process (Lakshmanan et al., 2015)

## Bulk Recovery of Rare Earth Elements

The PLS undergoes multiple stage solvent extraction to selectively remove Fe and other impurities (including U, Th, Cu, and Zn) followed by the recovery of Zr. A ketone and a tertiary amine (Alamine 336) in kerosene were used for the removal of Fe and impurities, respectively, while 2-ethylhexyl phosphonic acid mono-2-ethylhexylester (PC-88A) in kerosene was used for separation of Zr. Free hydrochloric acid was extracted from Zr raffinate with EXXAL™ 13, which can be recycled to the leaching stage. REEs+Y were precipitated from acid and Zr extracted raffinate with 10% oxalic acid at pH 2.0. Around 99% of the REEs+Y were precipitated at room temperature. Results are shown in Table 2. The rare earth oxalate obtained was washed with water, dried, calcined, and dissolved in hydrochloric acid to give a REEs+Y concentrate for individual separation by solvent extraction.

Table 2 – Results on REEs+Y precipitation from Zr raffinate with 10% oxalic acid

	Fe	Zr	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
Zirconium raffinate, mg/L	0.5	5	768	1550	174	612	146	8	152	30
REEs+Y ppte filtrate, mg/L	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
Zirconium raffinate, mg/L	208	41	115	15	71	8	772	1	2	<0.05
REEs+Y ppte 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
Zirconium raffinate, mg/L	1	1170	8750	915	58700	172	1590	123	9	125
REEs+Y ppte filtrate	<0.02	1710	7860	1320	66700	160	2140	121	17	155

Alternatively, PRO has tested the use of D2EHPA with EXXAL™ 13 in kerosene for direct extraction of REEs+Y from Zr raffinate after acid extraction (Table 3). Pregnant strip solution of REEs+Y could potentially be used as a feed for the individual separation of REEs+Y via solvent extraction process steps such as the separation process developed by Innovative Metals Corp. 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 extraction from acid-extracted Zr raffinate (mg/L)

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm
Zr Raffinate after acid extraction	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
Zr Raffinate after acid extraction	16	5	184	<5	<5	<5	7180	5710	<5	1610	4400	<5
REEs+Y Raffinate	<5	<5	<5	<5	<5	<5	6680	5630	<5	1470	4410	<5

## Separation of Rare Earth Elements

An individual REE separation process developed by Innovation Metals Corporation is being piloted in the state-of-the-art facility of Process Research ORTECH Inc. in Mississauga, Ontario, Canada. Feed solution to this pilot plant was prepared by dissolving a concentrated rare earth oxide mixture (>95% TREO) in hydrochloric acid solution. Impurities including Al and Fe were removed from the feed solution by precipitation. The solution was then adjusted to the proper pH for REE extraction. The elemental composition of this solution is presented in Table 4. Prior to pilot plant operation staging and input parameters were determined using a modelling program developed by Cytec Industries Inc. for rare earth separation using Cyanex 572. It was fed into pilot plant solvent extraction circuit 1 (SX1) for separation of

LREEs from HREEs. Solvent extraction of LREEs was carried out with an organic phase containing Cyanex 572 (50 % vol.) in kerosene followed by scrubbing and stripping with HCl. Prior to extraction the organic was saponified using 9.55M sodium hydroxide. A portion of the first circuit is shown in Figure 3.

Table 4 – Solvent extraction circuit 1 feed solution composition

	<b>La</b>	<b>Ce</b>	<b>Pr</b>	<b>Nd</b>	<b>Sm</b>	<b>Eu</b>	<b>Gd</b>	<b>Tb</b>
SX1 PLS, mg/L	26400	3700	6430	28800	6270	471	7145	839
	<b>Dy</b>	<b>Ho</b>	<b>Er</b>	<b>Tm</b>	<b>Yb</b>	<b>Lu</b>	<b>Y</b>	
SX1 PLS, mg/L	4560	659	1540	116	662	79.1	11000	



Figure 3 – One bank of the SX1 circuit

The SX1 circuit was operated continuously for 3484 hours over 6 months to determine suitable operating parameters as well as to produce solution for solvent extraction circuit 2 (SX2). By the end of operation, a raffinate purity of 99.8% and a strip solution purity of 99.9% were achieved. Metal distribution on the organic across the solvent extraction circuit is displayed in Figure 4. Raffinate and strip solution results are presented in Tables 5 and 6.

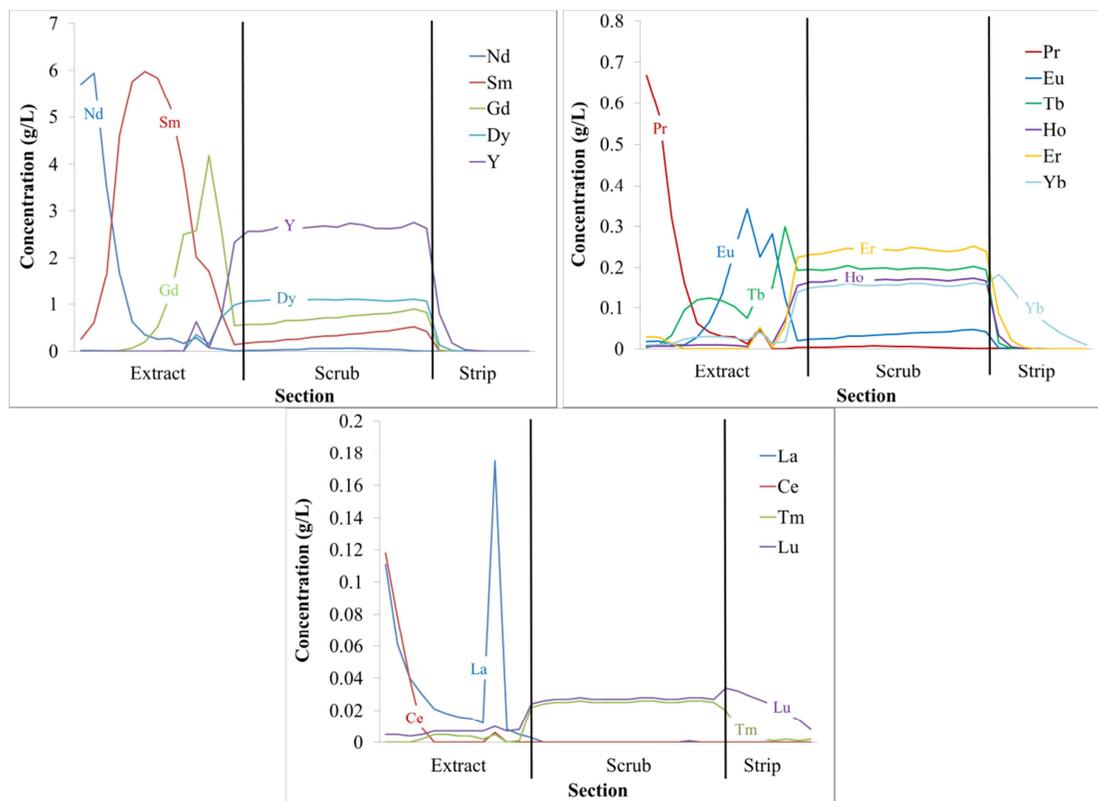


Figure 4 – Rare earth metals distribution on the organic phase across solvent extraction circuit 1

Using the strip solution produced in SX1 the SX2 circuit separated the Sm to Dy from the Ho to Lu plus Y. This circuit once again used Cyanex 572 (50 % vol.) in kerosene which was saponified using 4.775M sodium hydroxide. Operation took place for 5352 hours over 9 months due to operational issues and difficulty separating the Ho and Y from the Sm to Dy. Upon completion of operation a raffinate purity of 98.9% and a strip solution purity of 99.5% were reached. Results of SX2 operation presented in Figure 5 with raffinate and strip solution results are presented in Tables 5 and 6.

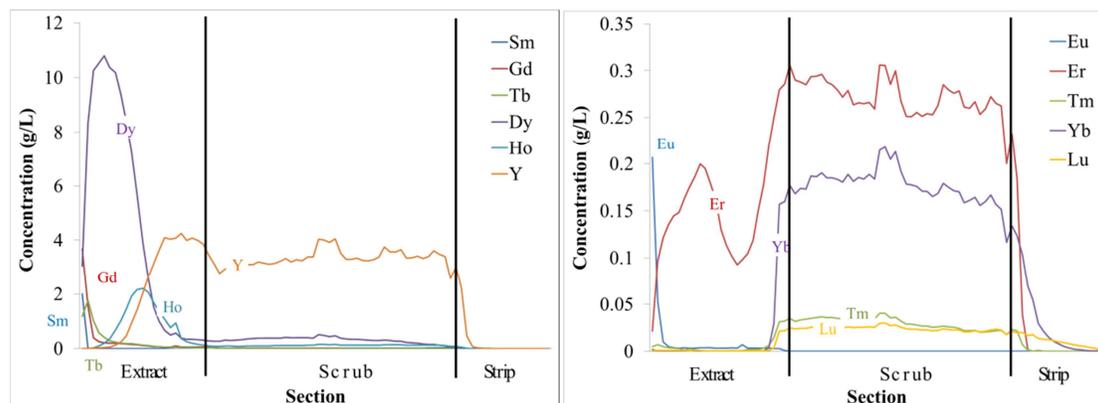


Figure 5 – Rare earth metal distribution on the organic phase across solvent extraction circuit 2

Solvent extraction circuit 3 (SX3) was fed using the raffinate from SX2 in which the Sm to Gd are separated from the Tb and Dy. Extraction was completed using Cyanex 572 (50 % vol.) in kerosene which

was saponified using 4.775 M sodium hydroxide. Operation of SX3 consisted of 1515 hours over 3 months with a raffinate purity of 98.5% and a strip purity of 98%. Results of SX3 are shown in Figure 6 with raffinate and strip solution results presented in Tables 5 and 6.

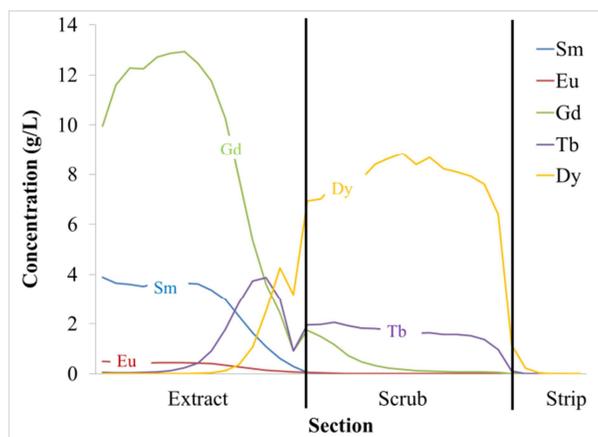


Figure 6 – Rare earth metal distribution on the organic across solvent extraction circuit 3

Using the strip solution produced from SX3, solvent extraction circuit 4 (SX4) was operated to separate the Tb from the Dy. Extraction was completed using Cyanex 572 (33 % vol.) in kerosene saponified using 4.775 M sodium hydroxide. In total, SX4 was operated for 1668 hours over 3 months to separate the Tb from the Dy. Based on the results presented in Figure 7; it can be observed that there was some instability present even near the end of operation. A Dy strip solution was produced with the goal of producing  $Dy_2O_3$ ; this would be completed by precipitating the Dy using oxalic acid and further calcining the oxalate to an oxide. Raffinate and strip solution results are presented below in Tables 5 and 6.

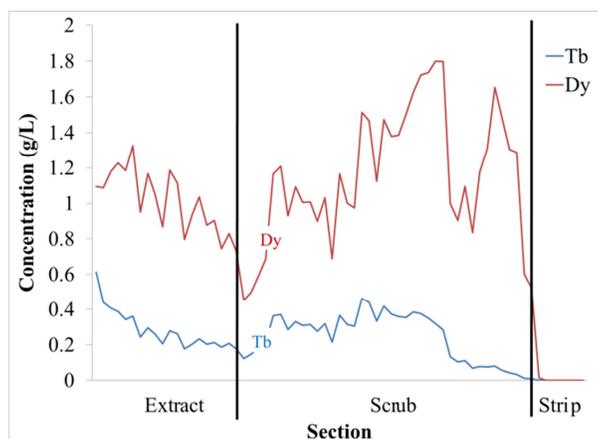


Figure 7 – Rare earth metal distribution on the organic across solvent extraction circuit 4

Table 5 – Solvent extraction circuit raffinate solution compositions

	<b>La</b>	<b>Ce</b>	<b>Pr</b>	<b>Nd</b>	<b>Sm</b>	<b>Eu</b>	<b>Gd</b>	<b>Tb</b>
SX1 Raffinate, mg/L	24600	3200	6200	29100	<5	26.9	<5	<5
SX2 Raffinate, mg/L	<5	<5	<5	20	10100	964	17800	2390
SX3 Raffinate, mg/L	45	<5	<5	138	8730	650	7620	<5
SX4 Raffinate, mg/L	<5	<5	<5	<5	<5	<5	6	1070
	<b>Dy</b>	<b>Ho</b>	<b>Er</b>	<b>Tm</b>	<b>Yb</b>	<b>Lu</b>	<b>Y</b>	
SX1 Raffinate, mg/L	<5	23.9	<5	<5	<5	<5	<5	
SX2 Raffinate, mg/L	2340	53	6	11	<5	<5	78	
SX3 Raffinate, mg/L	<5	<5	<5	6	<5	<5	39	
SX4 Raffinate, mg/L	578	<5	<5	<5	<5	<5	<5	

Table 6 – Solvent extraction circuit strip solution compositions

	<b>La</b>	<b>Ce</b>	<b>Pr</b>	<b>Nd</b>	<b>Sm</b>	<b>Eu</b>	<b>Gd</b>	<b>Tb</b>
SX1 Strip, mg/L	<5	<5	<5	17.1	6290	1750	11300	1560
SX2 Strip, mg/L	<5	<5	<5	<5	<5	6	<5	<5
SX3 Strip, mg/L	<5	<5	<5	<5	<5	<5	<5	1410
SX4 Strip, mg/L	<5	<5	<5	<5	<5	<5	<5	5
	<b>Dy</b>	<b>Ho</b>	<b>Er</b>	<b>Tm</b>	<b>Yb</b>	<b>Lu</b>	<b>Y</b>	
SX1 Strip, mg/L	7870	1010	1800	135	957	107	15700	
SX2 Strip, mg/L	106	203	2420	311	2060	273	17600	
SX3 Strip, mg/L	7460	76	<5	9	10	<5	70	
SX4 Strip, mg/L	4970	164	<5	<5	10	<5	125	

The importance of a complete separation of the rare earth elements becomes more and more apparent as the solvent extraction circuits progress. As concentrations decrease impurities have a greater impact. In terms of effect it is more difficult to remove a lighter rare earth element from the raffinate stream while heavier rare earth elements are more difficult to remove from the strip solution as was observed in SX3 and SX4 with regards to the Ho and Y. A flowsheet of the separations completed in the pilot plant is presented in Figure 8.

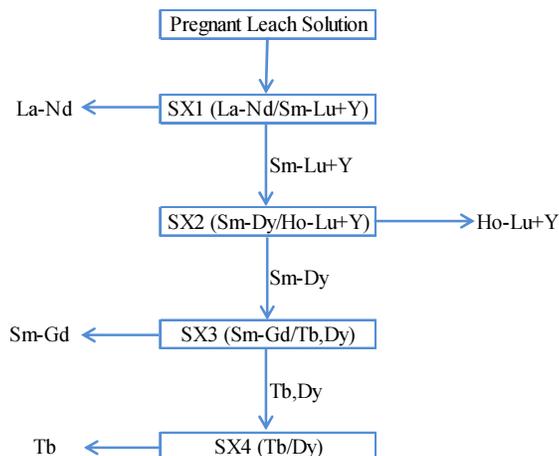


Figure 8 – Process flowsheet for the separation of REEs conducted in pilot plant

## CONCLUSIONS

Rare earth element ores are typically processed by leaching in acid, solvent extraction, precipitation of REEs+Y, re-dissolution of the REEs+Y precipitate in hydrochloric acid and separation of individual REEs+Y by solvent extraction. Process Research ORTECH Inc. (PRO) has developed an innovative process for the production of REEs using mixed chloride leach process. Extractions of REEs and REEs plus yttrium (REEs+Y) were 86.1% and 83.3%, respectively. A pilot plant campaign was conducted to separate the LREEs from the HREEs+Y followed by further separation of the HREEs. As the solvent extraction circuits progressed separation became more difficult due to the small separation factor between adjacent REEs. The solvent extraction purity results are shown in Table 7. By manipulating the operating parameters used on the solvent extraction circuits the purity of both raffinate and strip solution streams could be improved.

Table 7 – Solvent extraction solution purity (%)

	Raffinate	Strip
SX1	99.8	99.9
SX2	98.9	99.5
SX3	98.5	98

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