

SELECTIVE COUNTER CURRENT LEACHING AND OXALATE PRECIPITATION OF RARE EARTH ELEMENTS IN CHLORIDE MEDIA: THE CASE FOR BASTNASITE AND ANCYLITE MINERALS.

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ABSTRACT

Rare Element Resources Inc., a U.S. based company, has developed a three-stage process for producing a +98% mixed REO powder from hard rock feedstock (-48 mesh, 2.9-4.8% REO) consisting of bastnaesite and ancylite minerals. Firstly, the whole ore is digested in chloride media at low temperature in counter-current flow mode. Secondly, the rare earths (REEs) are selectively precipitated as oxalates directly from an impure pregnant leach solution (PLS). Finally, significant amounts of free acid and water are recovered from the REE-depleted filtrate and subsequently recycled within the process. Excess heat from the oxalate calcination process is captured and reused in the plant. Due to the low leach temperature (45°C) and moderate acid dosage (240-297 kg/t, HCl), rare earth oxides (REOs) are preferentially leached out of fine solids leaving most of the base metals (Ba, Fe, and Al) in the residue. Selective recovery of REEs from the PLS is achieved by mixing dilute oxalic acid (33% H₂C₂O₄) and PLS at elevated temperature (85-95°C). The REEs plus thorium are precipitated as oxalates (REE₂(C₂O₄).xH₂O) while the base metals are left behind in the barren filtrate. Multiple batch and pilot test results have confirmed that 50-80% of the oxalic acid can be recovered from the REE-depleted PLS through low-temperature crystallization (10-15°C). Typical leach efficiencies of critical rare earths at 45°C range from 85-99% (average 93%) while oxalate precipitation at high temperature increases the crystal size of RE oxalates (>450 microns, d80) thereby improving filtration. The economic benefits of this process include elimination of flotation and magnetic separation Capex and driving hydrometallurgical Opex down to \$6-7/kg, REO produced. As part of a comprehensive risk mitigation strategy, Rare Element Resources Inc has operated multiple pilot plants at SGS in Lakefield, Ontario, Canada to optimize counter-current leaching (CCL), REE oxalate precipitation (OXP), and thorium removal circuits. This paper presents pilot testing data from CCL and REE OXP circuits.

KEYWORDS

Rare Earths, Bastnaesite Minerals, Counter-current Leaching, Oxalate precipitation, Zero discharge

INTRODUCTION

Rare Element Resources, Inc. (RER) is developing the Bear Lodge Critical Rare Earth Project in northeastern Wyoming. The project consists of the *Bull Hill* deposit, the adjacent *Whitetail Ridge* deposit located NW of Bull Hill, a physical upgrade plant (PUG) located at the mine site, and a hydrometallurgical processing plant, located 40 miles southeast near an existing industrial park near the town of Upton, Wyoming, USA. The US Department of Energy ("Critical Materials Strategy" report, 2011), reviewed rare earths on the basis of their role in the clean energy sector as well as supply risk. They identified Neodymium (Nd), Europium (Eu), Terbium (Tb), Dysprosium (Dy), and Yttrium (Y) as critical rare earths (CREE) for both the short and long term.

Mineralogy

The Bull Hill resource has variable assemblage of ore minerals. REE mineralogy over the main dike zone at Bull Hill is dominated by REE fluorocarbonates, with a significant cerianite component at shallower levels. With increasing depth, ancylite becomes an important constituent of the REE mineral budget. The Whitetail Ridge resource is strongly REE fluorocarbonate-dominant, with some significant zones of cerianite at shallower levels. At depth, the deposit is also fluorocarbonate dominant, with decreasing cerianite and slightly increasing ancylite, though ancylite abundances are not as high as at Bull Hill.

Ancylite appears to be the most important host for rare earths in unoxidized carbonatite. It is typically characterized by a coarser grain size distribution and a stubby, prismatic crystal habit that differs significantly from the finer, fibrous to acicular REE fluorocarbonates (Van Rythoven & Clark, 2014). It is commonly intergrown with tightly interlocking strontianite, barite, and/or calcite. Ancylite and strontianite are typically found together, with ancylite the more abundant of the two. This texture and size distribution causes a significant proportion of the ancylite to report to the coarser size fractions during physical processing. A crush-and-sieve physical upgrade process will not concentrate ancylite nearly as well as REE fluorocarbonates and other REE ore mineral phases. Ancylite is a hydrous REE carbonate, and leach kinetics should not much differ from REE fluorocarbonates, as was REE phosphates.

This paper presents leaching characteristics of bastnaesite and ancylite type of minerals from Bull Hill deposit. The ore was not beneficiated by flotation or magnetic separation. Rather, the +10 inch rocks were crushed down to nominal 2 inch size and screened to separate +2 inch fraction or coarse rejects (<3% TREO by wt/wt distribution) from -2 inch fraction (>97% TREO by wt/wt distribution) which was the feedstock to the leach process. The -2 inch bulk solids were crushed down to 100% passing 48 mesh prior to chloride acid leaching. Overall, 22% of the total mined ore is rejected to the +2 inch fraction while 78% of the mass is processed in the leach plant at <48 mesh particle size. The cost of size reduction is minimized through coarse leaching.

Process Development

During the last five years, the Bear Lodge project has advanced through significant resource expansion, development of proprietary process technologies, multiple pilot plant studies, and recent completion of a Preliminary Feasibility Study that confirmed the technical and economic merits of the project. A list of some of the patent-pending processes is shown below:

- U.S. P/Patent No. 62/062,704: 10/18/2014. Low Temperature Extraction of Rare Earths from Bastnaesite Ores.
- PCT/US/14/12153: U.S. P/Patent No. 61/754,420. 01/18/2013. Extraction of Metals from Metallic Compounds.
- U.S. P/Patent No. 62/074,608: 11/03/2014. Selective Separation of Individual Rare Earth Elements by Precipitation and Solvent Extraction.

The first proprietary process provides a platform for selective leaching of bastnaesite type of rare earth oxide and calcite minerals at moderately low temperature. The second proprietary process describes a technology for separating rare earth from base metals in leach solution using oxalate precipitation. In the rare earth industry, oxalic acid is often used to precipitate metals from pure solutions such as Solvent Extraction (SX) strip electrolytes from which impurities have already been removed or reduced. Alternatively, oxalic acid is contacted with a leach solution that has undergone previous purification steps to prevent co-precipitation of impurities or radionuclides. In the current proprietary process, the leach solution, without prior pre-purification steps, is contacted with oxalic acid under high temperature conditions (85-95°C) and high acidity (0.45-1.65M) to inhibit the co-precipitation of Fe II and Fe III, Mn, Al, Mg, Sr, U, Ra, Mg, Zn, Ba, Al, Pb, Na, Ti, Nb etc) and produce a 97.5% pure Rare Earth Oxalate product (with 2.5%.Th). Excess oxalic acid left in the barren filtrate is recovered by crystallization at low temperature. Low-temperature leaching assists in lowering the digestion of Fe III and Al, which are the largest consumers of oxalic acid.

Oxalic acid from rare earths may be recovered by a proprietary metathesis process using cheap sodium carbonate to convert rare earth oxalate solids to rare earth carbonate solids where sodium oxalate solution is a recyclable by-product.

Low-Temperature Leaching

The first proprietary process was designed to leach bastnaesite/ancylite minerals (Bull Hill deposit) in chloride media at low temperature (45°C) in a counter current flow mode. The novelty of this process lies in the ability to limit the leaching kinetics of gangue minerals from the coarse solids (-48 mesh) while preferentially leaching valuable critical rare earth oxides (CREOs) at a low acid dosage. In this study, the REE ore was screened at a 2 inch cut-off size to reject the sterile coarse particles (+2 inch). The remaining -2 inch was stage crushed down to -48 mesh to constitute the feed to chloride leach reactors.

REE Purification

This paper also presents a proprietary process whereby REEs in chloride media are precipitated directly from the impure PLS containing excess base metals. The novelty of the process lies in the ability to recover REEs from highly acidic chloride solutions (0.5-1.5 M) and at fairly high temperature. Bastnaesite ores contain significant amounts of barium minerals which are readily soluble in hydrochloric acid solution. Also, at low temperature (<50°C), significant amounts of barium will co-precipitate with radionuclides (Ra226) and the rare earths to form a mixed oxalate product. However, at high temperature (>85°C), barium along with other base metals (Fe, Al, Mg, K, Na, Sr, Ca, U, and Mn) are strongly inhibited from crystallizing as oxalates. A combination of strong acidity and high temperature helps to control the purity of the final RE oxalate product. Ferric iron forms complex soluble oxalate anions and therefore consumes a significant quantity of oxalic acid. In this study, leach efficiency of iron ranged between 23% and 96% in the temperature range of 45-55°C. Additional benefits of this oxalic acid precipitation is that oxalic acid ($2\text{H}^+ \text{C}_2\text{O}_4^{2-}$) introduces protons (H^+) into the PLS, helping to build up HCl in the barren filtrate. The rare earth chlorides (RECl_3) consume $\text{C}_2\text{O}_4^{2-}$ radicals and free up chloride ions (Cl^-). This excess HCl acid in the barren PLS is recoverable by vaporization, along with water. Also, the act of vaporization upgrades the concentration of oxalic acid left in the distillation residual liquor, making crystallization possible at 10-15°C.

PILOT TESTING

Integrated Leach and Oxalate Precipitation Circuit

A pilot testing campaign was successfully carried out for 5 days (103.6 hours of actual run time) in order to process a composite sample from the Bear Lodge deposit (Bull Hill). Three unit operations were tested: counter-current leaching, REE oxalate precipitation, and hydrochloric acid recovery from

precipitation filtrate (the latter is not included in this paper). A schematic diagram of the integrated hydrometallurgical process circuit is shown in Figure 1.

Counter-Current Leaching (CCL)

The objective of the CCL circuit was to extract REE from the concentrate using hydrochloric acid as lixiviant. The control strategy in this circuit was based on feed flow rate and acid dosage; the concentrate feed rate was set based on the plant design and the acid flow rate was based on acid dosage (tonne of acid per tonne of concentrate). Motivated by the desire to lower acid consumption, it was necessary to establish a circuit configuration that minimized free acid in the final leach solution with high overall leach efficiencies. Also, the REE oxalate precipitation circuit was designed to operate within an acid range of 0.8-1.0 M HCl. After a series of bench scale scoping tests, it was determined that a counter-current flow would be the most suitable configuration to achieve these objectives. The counter-current leach process consisted of pre-leach and leach units.

Pre-Leach Circuit

The circuit consisted of a feed drum, a cascading tank-train of three glass reactors in series followed by two parallel filtration funnels, and a reservoir for hydrochloric acid addition. Each 3.8 L glass reactor was equipped with a 1/5-HP overhead agitator equipped with two pitch-blade type Teflon-coated impellers and a lid. Temperature was automatically controlled in all tanks and heating was supplied by electric heating mantles. All tanks were connected to reflux condensers; any condensate collected in the condenser would return back into its respective tank. Each tank was also connected to a main fume-collector which was connected to the building scrubbing system.

Leach Circuit

The circuit consisted of a feed tank, a cascading tank train of four glass reactors in series followed by two filtration funnels, and various reservoirs for hydrochloric acid addition.

Feed to Counter-Current Leach Cascade

Two 12-hour composite samples from the concentrate were collected each day throughout all of the campaigns. The average concentrate compositions are tabulated in [Table 1](#). Average REE grade was 2.63% (equivalent to 3.08% REO); average grades of relevant elements were: 1260 g/t Pr, 4324 g/t Nd, 153 g/t Eu, 80 g/t Dy, 27.5 g/t Tb, and 207 g/t Y. LREE (La, Ce, Pr, and Nd) represented 94% of the total REE. The feed particle size was < 48 mesh.

Table 1 –Average Composition of Concentrate Batches on daily basis

Date	LREE g/t	MREE g/t	HREE g/t	Th g/t	U g/t	Al %	Ba %	Ca %	Fe %	K %	Mg %	Mn %	Na %	P %	Pb %	Si %	Ti %	Zn %
Feb-10 PM	21400	1037	303	335	67.6	6.78	0.71	3.44	7.46	8.57	0.65	1.84	0.17	0.29	0.10	20.6	0.54	0.17
Feb-11 AM	26690	1285	378	421	69.0	6.46	0.76	3.82	8.01	7.32	0.76	2.04	0.18	0.33	0.12	19.2	0.55	0.18
Feb-11 PM	24400	1178	350	393	81.6	6.00	1.05	3.18	10.0	7.82	0.57	2.86	0.15	0.28	0.13	18.5	0.73	0.21
Feb-12 AM	25070	1213	368	400	78.0	6.61	0.90	3.66	8.72	8.6	0.65	2.31	0.14	0.28	0.11	19.3	0.58	0.18
Feb-12 PM	27330	1326	366	410	85.7	6.16	1.00	3.51	9.58	7.81	0.67	2.73	0.15	0.31	0.13	18.6	0.69	0.21
Feb-13 AM	24870	1186	340	385	80.2	6.30	0.74	3.68	8.93	7.96	0.67	2.34	0.15	0.30	0.12	19.1	0.59	0.19
Feb-13 PM	24860	1190	352	394	75.4	6.35	0.73	3.54	8.45	7.75	0.67	2.37	0.16	0.29	0.11	19.2	0.56	0.19
Feb-14 AM	24090	1119	350	384	66.8	6.75	0.73	3.54	8.07	8.24	0.68	1.97	0.15	0.30	0.11	20.1	0.55	0.17
Feb-14 PM	23850	1195	355	390	78.2	6.74	0.69	3.49	7.37	8.66	0.67	1.83	0.16	0.28	0.10	20.3	0.52	0.16
AVERAGE	24729	1192	351	390	75.8	6.46	0.81	3.54	8.51	8.08	0.67	2.25	0.16	0.30	0.11	19.4	0.59	0.18
MIN	27330	1326	378	421	85.7	6.78	1.05	3.82	10.00	8.66	0.76	2.86	0.18	0.33	0.13	20.6	0.73	0.21
MAX	21400	1037	303	335	66.8	6.00	0.69	3.18	7.37	7.3	0.57	1.83	0.14	0.28	0.10	18.5	0.52	0.16
REVSTD	7%	7%	6%	6%	9%	4%	17%	5%	11%	6%	7%	16%	7%	6%	9%	4%	12%	10%

Constant Parameters in Leach Process

The start-up set-points of the CCL circuit are included in Table 2. Acid dosage is a result of all acid streams added to leach tank L1. Acid dosage is expressed in kilograms of 100% HCl per tonne of dry

Pre-Leach feed concentrate. The designed retention times for the Pre-Leach and Leach circuits were 4 hours each. The target pulp densities for the first tank of each circuit were between 16-22% solids. Due to unavoidable variability of intermediate recycle streams (not shown), reticulation pump flows, retention time (not shown) nor pulp density during initial unsteady state conditions, only the initial targets are shown. During steady state conditions, these set points were achieved. Total acid dosage does not imply consumption but includes a huge component of recycled streams. Temperature range was 45-55°C and feed pulp density range was 22-40%.

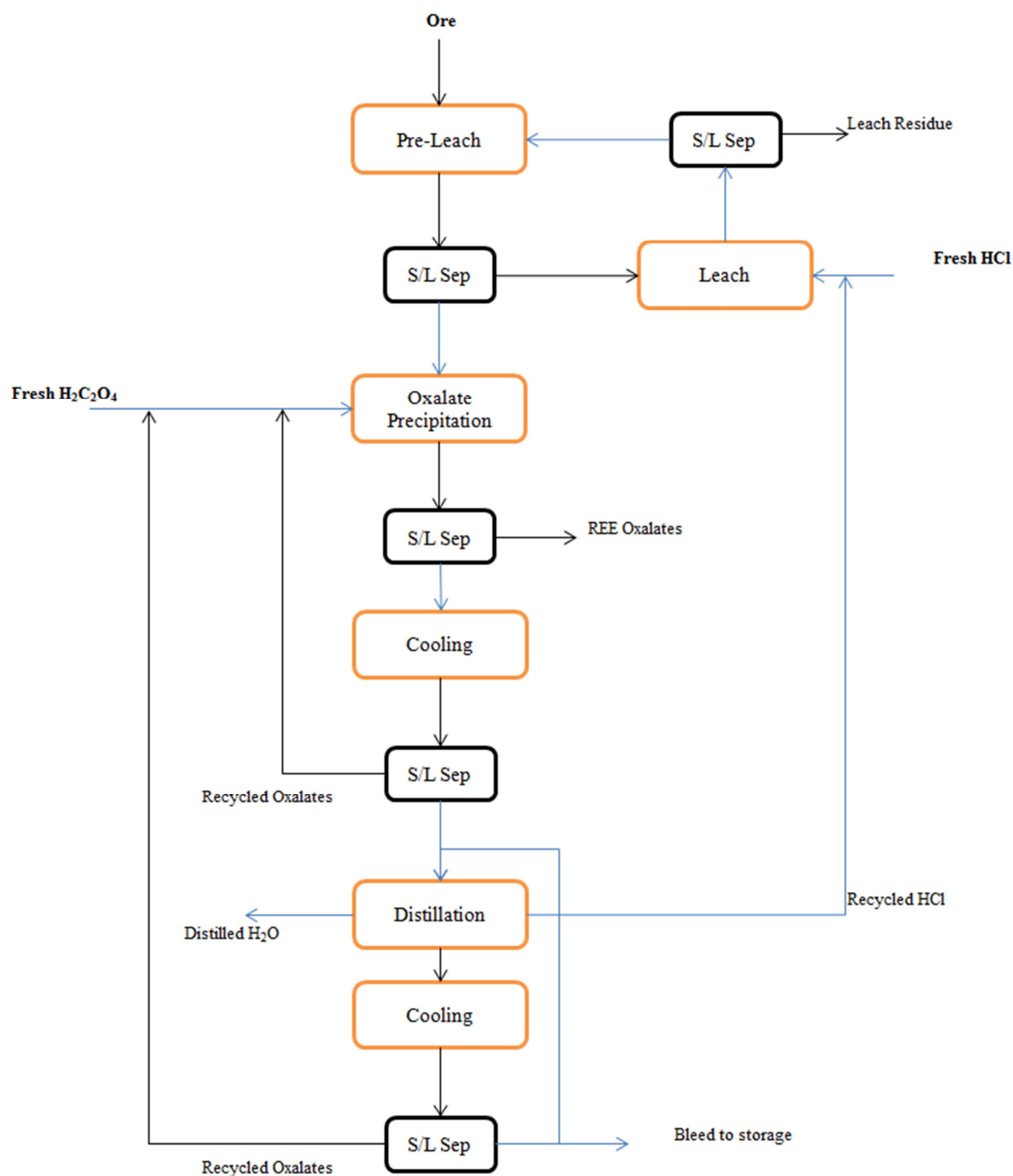


Figure 1 – Integrated Leach and Oxalate Precipitation Circuit

Table 2 – CCL Targets or Start-Up Set Points

Parameter	Unit	PP5
Feed rate (Concentrate)	g/min	21.3
Concentrate Feed Pulp Density	% solids	40
Pre-Leach: Leach Acid Split		0:100
Leach Feed Pulp Density	% solids	30
L1 Acid Dosage	kg/t	580
Fresh HCl strength	% HCl	30
Distillate acid recycle	%	0
Temperature	°C	55

PILOT LEACH RESULTS

Pre-Leach Filtrate Composition

Two 12-hour composite samples from the pre-leach discharge were taken each day throughout all of the campaigns. Pre-leach filtrate compositions are shown in Table 3. Differences in base metal tenors, especially iron, are associated with the changes in the circuit temperature; at the start of the pilot campaign, temperature in both pre-leach and leach circuits was set at 55°C. However, during the campaign, this temperature set point was adjusted to 45°C in both circuits. Consequently, the leach efficiency of U, Al, Ba, Ca, Fe, Mn, Silica, P, Zn, and Al decreased significantly as evidenced by the minimum and maximum tenors in Table 3.

Table 3 – Pre-leach Discharge Filtrate Composition

Date	LREE mg/L	MREE mg/L	HREE mg/L	Th mg/L	U mg/L	Al mg/L	Ba mg/L	Ca mg/L	Fe mg/L	K mg/L	Mg mg/L	Mn mg/L	Na mg/L	P mg/L	Pb mg/L	Si mg/L	Ti mg/L	Zn mg/L
Feb-10 PM	4207	214	55	46.2	9.93	1020	0.17	7280	3880	970	884	2970	43	409	130	224	77.5	155
Feb-11 AM	4895	259	71	71.4	16.2	1690	0.30	7250	10700	1590	1310	7160	58	581	244	108	144	343
Feb-11 PM	6800	320	86	99.8	18.5	1960	<0.3	8840	13800	1940	1530	9160	66	719	338	40.3	183	414
Feb-12 AM	6748	329	92	90.8	18.0	2090	0.20	10900	16400	2020	1750	8260	73	752	326	61.4	172	409
Feb-12 PM	6428	325	90	83.9	14.5	1800	0.30	10600	10500	1680	1550	5210	65	695	284	87.5	146	306
Feb-13 AM	4363	226	62	50.2	9.03	1100	0.20	8940	4570	1020	954	1880	53	435	122	264	84.3	158
Feb-13 PM	4610	245	67	52.1	9.79	1120	0.50	9510	4080	1060	990	1880	55	446	128	296	78.2	154
Feb-14 AM	5501	281	76	66.8	11.3	1410	<0.2	10200	5530	1390	1300	4050	59	566	220	231	102	217
Feb-14 PM	4759	246	66	66.7	9.85	1260	<0.2	7730	4720	1270	1180	3460	51	530	203	215	101	190
AVERAGE	5368	272	74	69.8	13.0	1494	0.26	9028	8242	1438	1272	4892	58	570	222	170	121	261
MIN	6800	329	92	46.2	9.03	1020	0.17	7250	3880	970	884	1880	43	409	122	40.3	77.5	154
MAX	4207	214	55	99.8	18.5	2090	0.50	10900	16400	2020	1750	9160	73	752	338	296	183	414
REVSTD	19%	16%	17%	27%	29%	27%	39%	15%	57%	27%	23%	56%	15%	23%	38%	56%	34%	42%

Leach Discharge Solids Composition

Two 12-hour composite samples from the leach discharge were taken each day throughout the pilot campaigns. Leach residue compositions are shown in Table 4. Major base metal components in the leach residue were aluminum (7.7%), iron (6.1%), potassium (9.4%), and silicon (26%). Iron showed the same leaching characteristics as Ce at different leach temperature step points. Thorium values in the leach residue varied between 23.3 g/t and 150 g/t while uranium ranged from 11.2 g/t to 53.9 g/t.

Table 4 – Leach Discharge Residue REE Composition

Date	LREE g/t	MREE g/t	HREE g/t	Th g/t	U g/t	Al %	Ba %	Ca %	Fe %	K %	Mg %	Mn %	Na %	P %	Pb %	Si %	Ti %	Zn %
Feb-10 PM	1512	35	46	39.2	53.9	7.46	1.08	0.02	4.33	9.08	0.07	1.63	0.14	0.10	0.02	26.6	0.83	0.21
Feb-11 AM	926	37	26	23.3	11.2	8.40	1.34	0.03	0.76	10.4	0.06	0.13	0.17	0.04	0.01	29.5	0.80	0.06
Feb-11 PM	1341	59	58	49.4	24.7	7.69	1.18	0.02	2.04	9.13	0.08	0.09	0.17	0.05	0.01	27.8	0.71	0.07
Feb-12 AM	721	27	30	25.9	16.3	7.77	1.52	0.02	0.91	10.2	0.06	0.11	0.18	0.04	0.00	29.1	0.84	0.06
Feb-12 PM	3298	123	74	103	35.8	7.61	1.09	0.04	5.50	9.57	0.15	0.27	0.19	0.08	0.02	26.6	0.69	0.12
Feb-13 AM	3127	102	71	90.4	40.7	7.49	1.09	0.03	7.32	9.61	0.14	0.63	0.18	0.07	0.03	25.1	0.74	0.14
Feb-13 PM	3106	100	76	97.3	40.8	7.98	0.99	0.04	7.65	9.96	0.14	0.53	0.18	0.07	0.02	25.3	0.73	0.14
Feb-14 AM	4350	106	80	117	38.5	7.84	0.98	0.04	7.62	9.37	0.17	0.36	0.17	0.09	0.03	25.5	0.68	0.13
Feb-14 PM	4607	147	90	150	48.4	7.35	0.84	0.04	7.85	8.75	0.24	0.81	0.18	0.10	0.04	24.6	0.64	0.15
AVERAGE	2554	82	61	96.2	38.6	7.68	1.05	0.03	6.09	9.44	0.15	0.55	0.17	0.08	0.02	26.0	0.71	0.13
MIN	4607	147	90	23.3	11.2	7.35	0.84	0.02	0.76	8.75	0.06	0.09	0.14	0.04	0.00	24.6	0.64	0.06
MAX	721	27	26	150	53.9	8.40	1.52	0.04	7.85	10.4	0.24	1.63	0.19	0.10	0.04	29.5	0.84	0.21
REVSTD	57%	53%	38%	58%	41%	4%	18%	28%	61%	6%	48%	97%	8%	32%	60%	7%	10%	42%

Counter Current Leach Metal Extraction

Metal recoveries were calculated based on a “calculated head” method, which considers the streams leaving the system:

$$\text{Extraction (\%)} = \frac{\text{Metal in PLS (g)}}{\text{Metal in PLS (g)} + \text{Metal in residue (g)}} * 100 \quad \text{“Calculated head” method} \quad (1)$$

where:

PLS: Pre-leach filtrate

residue: Leach residue

feed: Pre-leach feed (concentrate)

The REE extractions in the Counter-Current Leach process can be seen in Table 5. Iron was followed closely in the CCL circuit due to its impact on oxalic acid consumption in the precipitation circuit. Iron extraction decreased steeply from 96% (55°C) to mid-20% (45°C) halfway through the campaign due to the combination of lowering acid dosage and temperature. Aluminum (27% to 7%), barium (28% to 7%), magnesium (97% to 73%) and manganese (99% to 65%) showed similar declines in extractions over the duration of the campaign. Calcium extraction was above 99% throughout the campaign regardless of the temperature and acid addition. Critical elements extractions during steady state conditions (297 kg/t at 45°C) were 89% Dy, 94% Eu, 96% Nd, 97% Pr, 93% Tb, and 86% Y. Iron extraction during this period was 44%.

Table 5 – Counter-Current Leach REE Extractions

	La %	Ce %	Pr %	Nd %	Sm %	Eu %	Gd %	Tb %	Dy %	Ho %	Y %	Er %	Tm %	Yb %	Lu %	Sc %	Th %	U %
Feb-10 PM	97%	91%	98%	98%	98%	97%	97%	97%	94%	88%	87%	85%	69%	78%	56%	10%	91%	63%
Feb-11 AM	99%	99%	99%	99%	99%	99%	99%	99%	98%	98%	98%	98%	95%	96%	89%	29%	98%	97%
Feb-11 PM	98%	96%	99%	99%	98%	97%	97%	96%	93%	92%	91%	91%	87%	88%	80%	16%	94%	85%
Feb-12 AM	99%	98%	100%	100%	99%	99%	99%	99%	98%	99%	96%	98%	93%	98%	85%	25%	97%	92%
Feb-12 PM	97%	86%	96%	96%	94%	93%	93%	91%	88%	86%	86%	84%	84%	80%	73%	12%	82%	69%
Feb-13 AM	97%	85%	97%	97%	95%	94%	94%	94%	90%	88%	86%	85%	83%	78%	70%	10%	83%	65%
Feb-13 PM	96%	81%	96%	96%	94%	93%	92%	88%	86%	83%	82%	80%	71%	74%	58%	8%	76%	57%
Feb-14 AM	95%	76%	95%	94%	93%	92%	92%	88%	84%	81%	80%	78%	78%	73%	64%	8%	75%	58%
Feb-14 PM	95%	75%	94%	94%	91%	91%	90%	86%	82%	83%	79%	77%	76%	72%	69%	7%	70%	53%
OVERALL	97%	86%	97%	97%	95%	94%	94%	92%	89%	88%	86%	85%	81%	80%	70%	12%	83%	69%
MIN	95%	75%	94%	94%	91%	91%	90%	86%	82%	81%	79%	77%	69%	72%	56%	7%	70%	53%
MAX	99%	99%	100%	100%	99%	99%	99%	99%	99%	99%	98%	98%	95%	98%	89%	29%	98%	97%
REVSTD	2%	11%	2%	2%	3%	3%	4%	5%	6%	7%	8%	9%	11%	16%	55%	12%	23%	

Table 6 shows the base metal extraction in the counter-current leach process along with loss of feed weight.

Table 6: Counter-Current Leach Base Metal Extractions and Weight Losses

Date	wt. loss %	Al %	Ba %	Ca %	Fe %	Mg %	Mn %	Si %
Feb-10 PM	64%	11%	12%	99%	55%	91%	71%	0.3%
Feb-11 AM	79%	27%	28%	100%	96%	97%	99%	1.0%
Feb-11 PM	58%	15%	18%	100%	83%	93%	99%	0.2%
Feb-12 AM	72%	21%	16%	100%	95%	97%	99%	0.2%
Feb-12 PM	43%	11%	11%	99%	51%	85%	92%	0.2%
Feb-13 AM	47%	10%	9%	100%	37%	84%	74%	0.7%
Feb-13 PM	39%	7%	7%	99%	23%	80%	65%	0.7%
Feb-14 AM	29%	8%	9%	99%	27%	79%	84%	0.5%
Feb-14 PM	8%	8%	11%	99%	27%	73%	72%	0.5%
OVERALL	47%	11%	12%	99%	47%	85%	86%	0.5%
MIN	8%	7%	7%	99%	23%	73%	65%	0.2%
MAX	79%	27%	28%	100%	96%	97%	99%	1.0%
REVSTD	46%	51%	48%	0%	54%	10%	16%	61%

PILOT OXALATE PRECIPITATION TESTING

Precipitation Circuit Set-up

A schematic diagram of the Precipitation Circuit flowsheet is shown in [Figure 2](#). The first portion of the circuit consisted of a series of four reactors (OP1 through OP4), followed by a vacuum pan filter. The first three reactors were heated, while the fourth was cooled. The first four reactors, in the order of material flow, are referred to as OP1, OP2, OP3, and OP4. The second part of the circuit consisted of a cooled reactor (referred to as OPC) followed by a second pan filter. Also, the circuit contained a stirred reservoir of oxalate slurry and a feed surge tank.

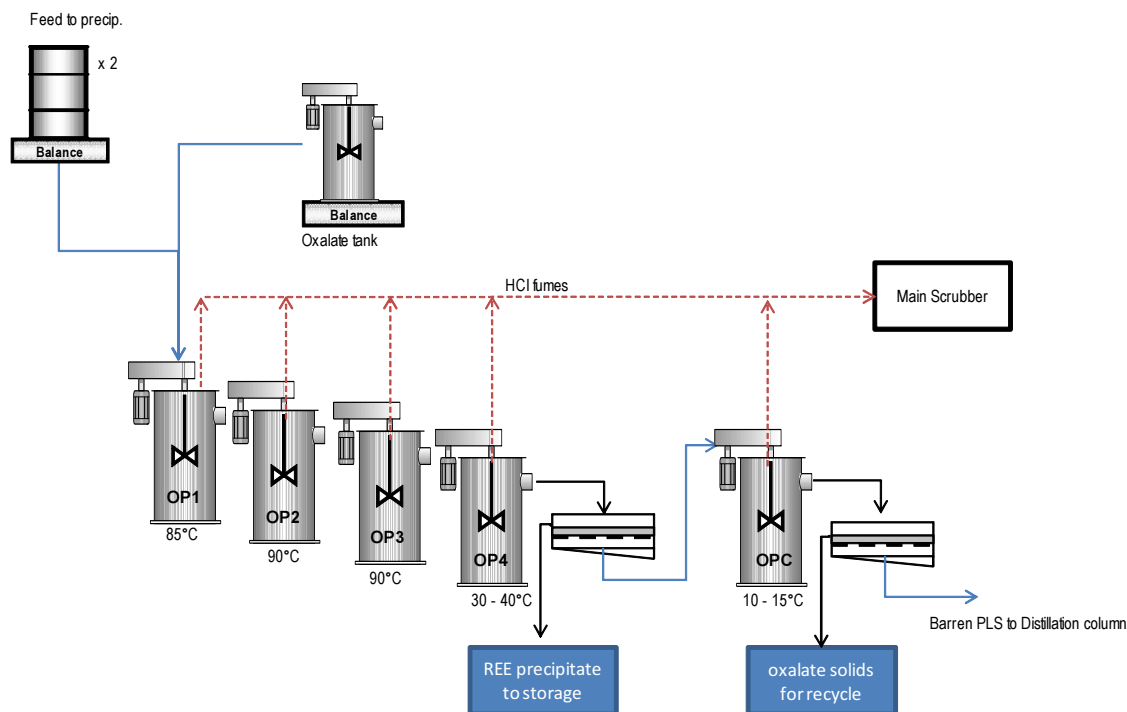


Figure 2: Precipitation Circuit Flowsheet

Precipitation Circuit Feed Streams

REE tenors in the Precipitation feed (Table 7) ranged from 3.95 g/L to 6.69 g/L; the difference in REE tenors is primarily associated with differences in HCl addition and CCL extractions. Main base metals

in the precipitation feed were iron (3.42-14.4 g/L), calcium (6.28-10.4 g/L), manganese (1.44-7.33 g/L), and aluminium (0.90-1.81 g/L). Differences in base metal tenors, especially iron, are associated with the changes in the CCL circuit temperature; at the start of the campaign temperature in both leach and pre-leach circuits was set at 55°C but during the campaign it was lowered to 45°C, decreasing base metal digestion and hence lowering the base metal tenors.

Table 7 – Precipitation Feed Average Composition

Date	LREE mg/L	MREE mg/L	HREE mg/L	Th mg/L	U mg/L	Al mg/L	Ba mg/L	Ca mg/L	Fe mg/L	K mg/L	Mg mg/L	Mn mg/L	Na mg/L	P mg/L	Pb mg/L	Si mg/L	Ti mg/L	Zn mg/L
Feb-11 AM	4341	222	59	59.8	14.6	1450	235	6280	8550	1440	1110	6360	59	532	213	140	123	307
Feb-11 PM	4966	231	63	73.3	13.4	1330	251	6420	9910	1300	1030	6810	47	502	235	41	132	294
Feb-12 AM	5922	286	79	79.1	15.8	1810	253	9280	14400	1740	1500	7330	64	650	288	60	154	365
Feb-12 PM	6291	316	87	82.7	14.3	1700	233	10400	10200	1580	1450	5120	63	684	283	91	145	299
Feb-13 AM	3881	199	55	48.7	8.57	976	116	7620	4780	889	831	2050	49	409	120	189	80.7	158
Feb-13 PM	3750	197	54	43.8	8.00	898	104	7940	3420	837	782	1440	48	375	104	256	65.9	126
Feb-14 AM	3743	188	50	51.4	7.65	980	148	6480	4020	971	905	2740	46	400	155	178	85.4	147
Feb-14 PM	4289	221	60	57.3	8.91	1100	168	7540	4700	1100	1020	3360	49	457	180	182	88.3	171
AVERAGE	4648	232	63	62.0	11.4	1281	189	7745	7498	1232	1079	4401	53	501	197	142	109	233
MIN	6291	316	87	43.8	7.65	898	104	6280	3420	837	782	1440	46	375	104	41.3	65.9	126
MAX	3743	188	50	82.7	15.8	1810	253	10400	14400	1740	1500	7330	64	684	288	256	154	365
REVSTD	21%	20%	20%	24%	30%	27%	33%	19%	52%	27%	25%	52%	14%	23%	35%	52%	30%	39%

PILOT OXALATE PRECIPITATION RESULTS

Precipitation Circuit Chemical Performance

The precipitation discharge liquor (filtrate) compositions can be seen in Table 8. The corresponding solid precipitate assays are summarized in Table 9. Halfway through the campaign, base metal impurity levels in the filtrate peaked, resulting in 10.9 g/L Fe, 8.6 g/L Ca, and 5.0 g/L Mn as a result of the high impurity levels in the feed during this period. These levels dropped significantly by the end of the campaign to 4.2 g/L Fe, 6.8 g/L Ca, and 3.1 g/L Mn. By the end of the campaign, the discharge solution contained 616 mg/L TREE, down from levels as high as 4.1 g/L seen partway into the campaign. Lanthanum and cerium comprised 89% of the REE in the barren solution. The precipitate product generated by the end of the campaign contained 44.6% TREE (96.2% of which were LREE) with the greatest impurities being 4970 g/t Th, 1.24% Ca, and 0.9% Si. Only one sample of the solids was sampled for oxalate, and found to contain 36.2% (as $C_2O_4^{2-}$)

Table 8 – Precipitation Circuit Discharge: Filtrate Compositions

Date	LREE mg/L	MREE mg/L	HREE mg/L	Th mg/L	U mg/L	Al mg/L	Ba mg/L	Ca mg/L	Fe mg/L	K mg/L	Mg mg/L	Mn mg/L	Na mg/L	P mg/L	Pb mg/L	Si mg/L	Ti mg/L	Zn mg/L
Feb-11 AM	889	15	10	0.41	10.2	1040	77	5470	5440	1030	841	4220	53	398	145	147	81	202
Feb-11 PM	2510	69	28	3.03	11.7	1330	184	5970	9420	1220	1020	5660	53	469	203	64	124	277
Feb-12 AM	3226	96	37	7.50	12.2	1290	240	6830	10900	1280	1060	6690	52	532	233	43	125	297
Feb-12 PM	3965	133	49	7.73	12.6	1540	196	8650	10500	1420	1300	5090	58	573	247	71	128	283
Feb-13 AM	991	12	10	0.22	8.36	1020	126	7110	5700	927	882	2620	48	422	141	133	87	179
Feb-13 PM	242	2	2	0.16	6.44	729	75	5410	3000	658	638	1180	41	304	64	210	53	105
Feb-14 AM	415	4	4	0.32	7.12	916	119	6670	3670	858	830	2220	1950	380	118	197	69	137
Feb-14 PM	604	5	6	0.16	7.78	1030	135	6850	4210	1010	955	3100	2080	431	165	169	81	165
AVERAGE	1605	42	18	1.82	9.06	1112	144	6620	6605	1050	941	3848	542	439	165	129	94	206
MAX	3965	133	49	0.16	6.44	729	75	5410	3000	658	638	1180	41	304	64	43	53	105
MIN	242	2	2	7.73	12.6	1540	240	8650	10900	1420	1300	6690	2080	573	247	210	128	297
REVSTD	89%	121%	95%	137%	25%	23%	41%	16%	48%	23%	21%	49%	168%	20%	37%	49%	31%	35%

Table 9 –Precipitation Circuit Discharge: Precipitate Elemental Assays

Date	LREE %	MREE %	HREE %	Th %	U %	Al %	Ba %	Ca %	Fe %	K %	Mg %	Mn %	Na %	P %	Pb %	Si %	Ti %	Zn %
Feb-11 AM	37.8	2.42	0.52	0.59	0.005	0.06	1.11	0.31	0.11	<0.40	0.007	0.004	<0.04	0.005	<0.03	0.22	0.03	0.003
Feb-11 PM	35.0	3.01	0.56	1.66	0.003	0.21	1.09	0.29	0.14	<0.40	0.011	0.010	<0.04	0.003	<0.03	0.84	0.04	0.006
Feb-12 AM	33.2	2.71	0.50	1.21	0.003	0.04	0.16	0.24	0.04	<0.40	0.002	0.001	<0.04	0.003	<0.03	0.18	0.02	0.006
Feb-12 PM	39.1	3.31	0.61	1.36	0.003	0.10	0.20	0.29	0.10	<0.40	0.012	0.003	<0.04	0.003	<0.03	0.34	0.03	0.007
Feb-13 AM	32.5	2.32	0.49	0.78	0.003	0.09	0.38	0.38	0.07	0.40	0.009	0.003	0.04	0.003	0.01	0.31	0.02	0.008
Feb-13 PM	25.0	1.47	0.38	0.35	0.001	0.02	0.02	1.13	0.01	<0.40	0.006	0.000	<0.04	0.003	<0.03	0.10	0.01	0.001
Feb-14 AM	34.2	1.76	0.51	0.34	0.002	0.03	0.03	0.48	0.07	<0.40	0.006	0.004	<0.04	0.003	<0.03	0.11	0.01	0.003
Feb-14 PM	41.7	2.33	0.60	0.50	0.004	0.03	0.04	1.24	0.02	<0.40	0.011	0.003	<0.04	0.003	0.02	0.09	0.02	0.002
AVERAGE	34.8	2.42	0.52	0.85	0.003	0.07	0.38	0.54	0.07	<0.40	0.008	0.004	<0.04	0.003	0.03	0.27	0.02	0.005
MAX	41.7	3.31	0.61	1.66	0.005	0.21	1.11	1.24	0.14	<0.40	0.012	0.010	<0.04	0.005	<0.03	0.84	0.04	0.008
MIN	25.0	1.47	0.38	0.34	0.001	0.02	0.02	0.24	0.01	0.40	0.002	0.000	0.04	0.003	0.01	0.09	0.01	0.001
REVSTD	15%	25%	14%	59%	32%	88%	121%	74%	66%	0%	42%	81%	0%	19%	31%	90%	36%	56%

Precipitation Circuit Efficiency

The overall precipitation efficiency within the Precipitation circuit was calculated using a modified form of the calculated head extraction formula:

$$\text{Precipitation}(\%) = \frac{\text{Metal in precipitates (g)}}{\text{Metal in precipitates (g)} + \text{Metal in filtrate (g)}} \times 100\% \quad (2)$$

The precipitation efficiencies for the REE and base metals can be seen in Tables 10 and 11. Precipitation efficiencies for critical elements during steady state conditions (90.4 g/L total oxalate) were 98% Dy, 99% Eu, 96% Nd, 95% Pr, 98% Tb, and 91% Y. Calcium precipitation was 6% during this period.

There is a very high Ca result on February 14, due to the recycle of oxalate solids recovered from the distillation residue. The residue contained a significant quantity of calcium oxalate that crystallized after cooling down. The temperature in the crystallizer was too low (sub-zero, when the target was 10-15°C) allowing calcium to precipitate as oxalates, polluting the product when they were recycled to the circuit.

Table 10 – REE Overall Precipitation Efficiencies

Date	La %	Ce %	Pr %	Nd %	Sm %	Eu %	Gd %	Tb %	Dy %	Ho %	Y %	Er %	Tm %	Yb %	Lu %	Sc %	Th %	U %
Feb-11 AM	51	60	69	74	81	81	81	80	76	73	61	68	64	62	67	63	96	2
Feb-11 PM	73	79	83	85	89	89	90	90	88	87	80	84	81	79	83	82	98	5
Feb-12 AM	44	56	65	69	80	81	80	79	76	72	55	67	60	58	64	60	97	2
Feb-12 PM	46	60	68	73	82	83	82	81	79	74	58	69	62	64	65	53	98	3
Feb-13 AM	41	58	68	75	86	87	86	85	80	73	55	67	58	58	66	57	99	2
Feb-14 AM	94	98	99	99	100	100	100	99	99	98	99	98	98	80	98	86	100	3
Feb-14 PM	77	89	95	96	99	99	98	98	98	96	91	95	80	94	79	85	100	3
AVERAGE	61	71	78	82	88	88	88	87	85	82	71	78	69	73	72	70	98	3
MAX	94	98	99	99	100	100	100	99	99	98	99	98	81	98	83	86	100	5
MIN	41	56	65	69	80	81	80	79	76	72	55	67	58	58	64	53	96	2
REVSTD	34%	24%	18%	15%	9%	9%	9%	10%	12%	14%	26%	18%	15%	23%	12%	21%	1%	34%

Table 11 – Base Metal Overall Precipitation Efficiencies

Date	Al %	As %	Ba %	Be %	Ca %	Fe %	K %	Mg %	Mn %	Mo %	Na %	P %	Pb %	Si %	Sr %	Ti %	V %	Zn %
Feb-11 AM	0.3	17	41	0	0.4	0.1	1.9	0.1	0.0	2.1	3.4	0.1	1.0	11	0.9	1.4	0.1	0.1
Feb-11 PM	1.4	36	65	0	2.0	0.3	5.0	0.4	0.0	3.6	7.3	0.5	3.7	34	3.3	5.8	0.9	0.3
Feb-12 AM	1.0	28	7	42	1.0	0.2	2.9	0.2	0.0	1.9	5.6	0.3	1.8	31	1.1	3.6	1.4	0.1
Feb-12 PM	0.7	29	7	29	0.6	0.1	3.3	0.2	0.0	2.4	6.5	0.3	2.0	30	0.7	3.6	0.4	0.2
Feb-13 AM	0.6	20	6	39	0.4	0.1	2.3	0.1	0.0	1.4	3.7	0.2	1.3	14	0.4	1.8	0.5	0.2
Feb-14 AM	1.6	36	10	42	22.4	0.4	6.6	0.1	0.1	17.0	0.7	0.3	24.2	10	3.9	7.0	2.0	0.8
Feb-14 PM	0.4	24	1	-	5.6	0.1	3.1	0.1	0.0	3.7	0.2	0.1	3.8	5	1.0	2.6	0.3	0.2
AVERAGE	0.9	27	20	26	4.6	0.2	3.6	0.2	0.0	4.6	3.9	0.3	5.4	19	1.6	3.7	0.8	0.3
MAX	1.6	36	65	42	22.4	0.4	6.6	0.4	0.1	17.0	7.3	0.5	24.2	34	3.9	7.0	2.0	0.8
MIN	0.3	17	1	0	0.4	0.1	1.9	0.1	0.0	1.4	0.2	0.1	1.0	5	0.4	1.4	0.1	0.1
REVSTD	57%	26%	121%	78%	174%	65%	46%	61%	152%	122%	70%	62%	155%	61%	87%	55%	86%	91%

CONCLUSIONS

Overall

An integrated hydrometallurgical pilot plant was successfully operated for 5 days using a feed concentrate from the Bear Lodge deposit. The feed solids to the process contained 3.08% REO and the final product was a 98% pure REO bulk concentrate or RE oxalate precipitate cake. The overall individual recoveries of critical rare earths were: 87% Dy, 93% Eu, 95% Nd, 95% Pr, 89% Tb, and 81% Y. The overall recovery of REEs averaged 86%. Low temperature counter current leaching was found to be effective in selectively extracting REEs from bastnaesite/ancylite ores. The oxalate precipitation route was quantitatively proven as an excellent tool for separating REEs from base metals without the need to pre-treat the PLS.

Leach Process

REE extraction in the counter current leach step ranged from 85% to 99% (averaging 93%). The extraction of critical rare earth elements during steady state conditions (297 kg/t HCl addition at 45°C) were 89% Dy, 94% Eu, 96% Nd, 97% Pr, 93% Tb, and 86% Y. Iron extraction during this period was 44%

Oxalate Precipitation Process

The precipitation efficiency of critical REE elements during steady state conditions (90.4 g/L total oxalate) were 98% Dy, 99% Eu, 96% Nd, 95% Pr, 98% Tb, and 91% Y. Oxalate were recycled during this campaign. The final product of the plant generated during the steady state conditions contained 44.6% TREE (96.2% of which were LREE) with the greatest impurities being 4970 g/t Th, 1.24% Ca, and 0.9% Si. Efficient PLS filtration prior to REE precipitation and optimized crystallization of oxalates from barren PLS are necessary process steps to lower calcium and silicate impurities in the final product.

REFERENCES

Ray, J., Van Rythoven, A., & Clark, J. (2014). Mineralogical Modeling of Bull Hill and White Ridge Deposits. Rare Element Resources Inc., Internal RER Report.