



# NETL Life Cycle Inventory Data

## Process Documentation File

**Process Name:** Separation of rare earth elements using ion exchange  
**Reference Flow:** 1 kg of mixed rare earth chloride hexahydrate  
**Brief Description:** Separation of rare earth chlorides in solution using ion exchange

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### Section I: Meta Data

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**Geographical Coverage:** N/A **Region:** N/A  
**Year Data Best Represents:** N/A  
**Process Type:** Manufacturing Process (MP)  
**Process Scope:** Gate-to-Gate Process (GG)  
**Allocation Applied:** No  
**Completeness:** All Relevant Flows Captured

#### Flows Aggregated in Data Set:

Process  Energy Use  Energy P&D  Material P&D

#### Relevant Output Flows Included in Data Set:

Releases to Air:  Greenhouse Gases  Criteria Air  Other  
Releases to Water:  Inorganic  Organic Emissions  Other  
Water Usage:  Water Consumption  Water Demand (throughput)  
Releases to Soil:  Inorganic Releases  Organic Releases  Other

#### Adjustable Process Parameters:

recovery\_rate [kg/kg] kf of separated rare earth chloride hexahydrate per kg of rare earth chloride hexahydrate input  
Ce *[binary] Parameter to select cerium as the output*  
La *[binary] Parameter to select lanthanum as the output*

Pr	<i>[binary] Parameter to select praseodymium as the output</i>
Nd	<i>[binary] Parameter to select neodymium as the output</i>
Sm	<i>[binary] Parameter to select samarium as the output</i>
Eu	<i>[binary] Parameter to select europium as the output</i>
Gd	<i>[binary] Parameter to select gadolinium as the output</i>
Tb	<i>[binary] Parameter to select terbium as the output</i>
Dy	<i>[binary] Parameter to select dysprosium as the output</i>
Ho	<i>[binary] Parameter to select holmium as the output</i>
Er	<i>[binary] Parameter to select erbium as the output</i>
Tm	<i>[binary] Parameter to select thulium as the output</i>
Yb	<i>[binary] Parameter to select ytterbium as the output</i>
Lu	<i>[binary] Parameter to select lutetium as the output</i>
Y	<i>[binary] Parameter to select yttrium oxalate as the output</i>
Electricity_f	[kWh/kg] Wh electricity per kg of rare earth concentrate input
Soln_conc	[g/L] kg of HEDTA/EDTA/Rare earth per kg of rare earth chloride co

### Tracked Input Flows:

Rare Earth Chloride Concentrate	<i>[Technosphere] Reference flow rare earth chloride solution</i>
Electricity	<i>[Technosphere] Electricity</i>
Ion Exchange Resin	<i>[Technosphere] Ion exchange resin used for isolation of rare earth elements</i>
Hydrochloric Acid	<i>[Technosphere] Hydrogen chloride used prior to process for elution as a rinse</i>
HEDTA	<i>[Technosphere] Acid solution used to separate HREEs</i>
Ammonium-EDTA	<i>[Technosphere] Acid solution used to separate LREEs</i>
Heat	<i>[Technosphere] Heat energy</i>

**Tracked Output Flows:**

separated rare earth chloride hexahydrate	<i>[Intermediate product] separated rare earth chloride hexahydrate</i>
Ammonium_out	<i>Emission to Water</i>
EDTA	<i>Liquid waste - water, ammonium, Ion Exchange Resin [Waste for disposal]</i>

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**Section II: Process Description**

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**Associated Documentation**

This unit process is composed of this document and the data sheet (DS) *DS\_Stage1\_O\_Rare\_Earth\_Ion\_Exchange\_2014.01.xlsx*, which provides additional details regarding relevant calculations, data quality, and references.

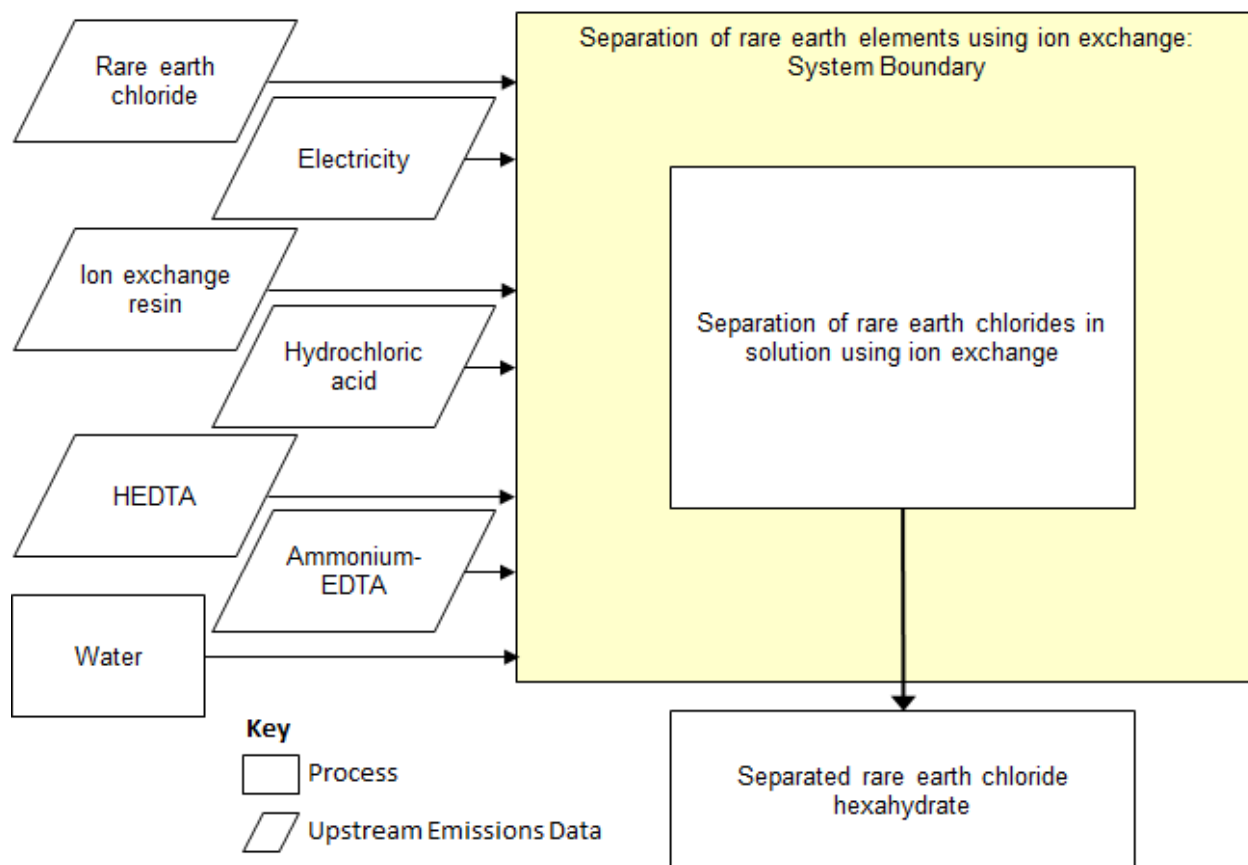
**Goal and Scope**

This unit process provides a summary of relevant input and output flows associated with selectively adsorbing rare earth metals on an ion exchanger and fractionally eluting them with an aqueous solution of a chelating agent (EDTA or HEDTA) by using ion exchange with a sulfonic resin. The reference flow of this unit process is: 1 kg of separated rare earth chloride hexahydrate.

**Boundary and Description**

This unit process accounts for electricity use for pumping the solutions, chemical use for the loading and separation phases; solid waste from the sulfonic resin; and water and hydrochloric acid use to stimulate the ion exchange reactions. **Figure 1** provides an overview of the boundary of this unit process.

Figure 1: Unit Process Scope and Boundary



To increase differences in the basicity of adjacent rare earths, various complexes are formed by individual rare earths in the mixture through the use of chelating agents (complexing agents) such as ethylene di-amine tetra-acetic acid (EDTA) and 2-hydroxy ethylene diamine triacetic acid (HEDTA) (Gupta & Krishnamurthy, 2005). Ion exchange (IX) is noted for its simplicity and its ability to produce high purity rare earths, but the process is very slow and is not continuous. Consequently, IX has become largely outdated in favor of solvent extraction even though it is still regarded as superior for the production of extremely pure materials (Kolodynska & Hubicka, 2012).

The IX process has minimal operational energy demands and typically only requires electricity to operate small pumps for pumping fluids under low hydraulic pressure (Drewes, Cath, Xu, 2009). Electricity use for pumping is calculated based on the theoretical work required to provide a pump head of 5 m and 80% efficiency (Drewes, Cath, Xu, 2009), drawing 1.5 kilowatt (kW) electricity per kilogallon (kgal). Applying this energy demand to our scenario, of a flow velocity of 2mL/min, with approximately 1L of solution per rare earth element, it was estimated that 0.001050 Wh electricity would be required per kg rare earth separated through IX, on average.

For the rare earth resin, this process uses a sulfonic resin (Sparks & Lindstrom, 1971). There are many sulfonic commercial resins available and the supplier should not change

the amount of rare earth element recovered or IX efficiency. IX resin is reusable, but must be replaced periodically, resulting in a total ion exchange resin consumption rate of 0.0001 kg resin per kg rare earth oxalate produced. For our process, we counted it as solid (nonhazardous) waste (Drewes, Cath, Xu, 2009). Generally, sulfonic resin spheres are approximately 0.1 mm (0.004 inch) diameter, are packed into a long column, and the resin bed is prepared by passing 0.2 kg of 6M HCl through the loading column (Ozturk, 2003). Water (0.15 kg) is then passed through the column to rinse the HCl (Ozturk, 2003).

The feedstock is a mixed Rare Earth Chloride ( $\text{RECl}_3$ ) hexahydrate ( $6 \text{ H}_2\text{O}$ ) solution based on the composition of 1 kg of Mountain Pass bastnaesite (Gupta & Krishnamurthy, 2005; Sparks & Lindstrom, 1971). The pH of the solution is 8.3 (Moore, 2000) (Spedding, Wheelwright, Powell, 1957).

The columns are heated to and maintained at 92 °C to maintain the acid form of EDTA. The 0.5% ammonium EDTA (complexing agent) and 0.5% HEDTA (which uses  $\text{H}^+$  as the retaining ion) solutions are added to the  $\text{RECl}_3$  solution (Lindstrom, 1966; Moore, 2000). The retaining ion is needed to prevent the first rare earth ion from spreading out and being lost during the separation process (Gupta & Krishnamurthy, 2005).

The solutions are passed continuously through resin-packed glass columns and kept at a steady flow of 2ml/min (Moore, 2000; Kolodynska & Hubicka, 2012). The effluent is then traditionally collected in fractions of 15ml from which oxalates are precipitated and converted to oxides (Sparks & Lindstrom, 1971) (Gupta & Krishnamurthy, 2005) (Kolodynska & Hubicka, 2012). In our process, we added  $6.08 \times 10^{-4}$  kg of 6M HCl solution (in 1L water) to convert the 8.3 pH solution to a pH of 1.0 to separate rare earth elements and transform into  $\text{RECl}_3$ . EDTA precipitates out and  $\text{RECl}_3 \cdot 6\text{H}_2\text{O}$  is the output (Moore, 2000).

Essentially all of the HEDTA and most of the EDTA from ammonia-EDTA can be recaptured at the end of the process by allowing them to precipitate (Lindstrom, 1966). The demand for these two acids are then based on a 1:1 ratio with rare earth content which are reduced by the amount recovered (100% for HEDTA and 85% for EDTA) (Lindstrom, 1966).

The amount of water input for the process is calculated based on achieving the concentration of EDTA noted above. This water demand is then used to calculate the heat required to increase the temperature of the solution from 20 °C to 92°C, using the specific heat of water. The liquid waste is made up primarily of this water. Unless the water is sent to a water processing unit process, the water consumption for the overall ion exchange process will remain higher than what is likely to happen in practice.

**Table 1** provides a summary of modeled input and output flows. Additional detail regarding input and output flows, including calculation methods, is contained in the associated DS. Note that the only quantity that will change is the quantity of separated rare earths, so only the results for cerium output are shown.

Table 1: Unit Process Input and Output Flows

Flow Name	Value	Units (Per Reference Flow)
<b>Inputs</b>		
<b>Rare Earth Chloride Concentrate</b>	<b>5.60E-01</b>	<b>kg</b>
<b>Electricity</b>	<b>4.24E+00</b>	<b>Wh</b>
<b>Ion Exchange Resin</b>	<b>1.00E-03</b>	<b>kg</b>
Water	2.49E+02	kg
<b>Hydrochloric Acid</b>	<b>1.51E-01</b>	<b>kg</b>
<b>HEDTA</b>	<b>0.00E+00</b>	<b>kg</b>
<b>EDTA</b>	<b>1.87E-01</b>	<b>kg</b>
<b>Heat</b>	<b>7.29E+04</b>	<b>kJ</b>
<b>Outputs</b>		
<b>separated rare earth chloride hexahydrate</b>	<b>5.60E-01</b>	<b>kg</b>
Liquid waste, to treatment	2.50E+02	kg
Ion Exchange Resin [Waste for disposal]	1.00E-03	kg

\* **Bold face** clarifies that the value shown *does not* include upstream environmental flows.

### Embedded Unit Processes

None.

### References

- Gupta, C.K. and Krishnamurthy, N. (2005). Extractive Metallurgy of Rare Earths. Boca Raton, FL: CRC Press.
- Jörg E. Drewes, Tzahi Y. Cath, Pei Xu. (2009). An Integrated Framework for Treatment and Management of Produced Water: Technical Assessment of Produced Water Treatment Technologies. Colorado School of Mines: Colorado. RPSEA Project 07122-12. Retrieved June 27, 2014 from [http://aqwatec.mines.edu/produced\\_water/treat/docs/Tech\\_Assessment\\_PW\\_Treatment\\_Tech.pdf](http://aqwatec.mines.edu/produced_water/treat/docs/Tech_Assessment_PW_Treatment_Tech.pdf)
- Kołodziejńska D., Hubicka, H. (2012) Investigation of Sorption and Separation of Lanthanides on the Ion Exchangers of Various Types. Ion Exchange Technologies. Retrieved June 20, 2014 from <http://dx.doi.org/10.5772/50857>
- Lindstrom, Roald E. (1966) Process for Separating Rare-Earth Elements by Ion Exchange. U.S. Patent 3,228,750. Washington, DC: US. Retrieved June 19, 2014 from <http://www.google.com/patents/US3228750>
- Moore, Bruce W. (2000) Selective Separation of Rare Earth Elements by Ion Exchange in an Iminodiacetic Resin. U.S. Patent 6093376. Washington, DC: US. Retrieved June 17, 2014 from <http://www.google.com/patents/US6093376>

Ozturk, Sema. (2003). Use of Solid Phase Extraction for Preconcentration of Rare Earth Elements: Provence Studies in Çatalhoyuk obsidians. Retrieved June 27, 2014 from <http://etd.lib.metu.edu.tr/upload/1206655/index.pdf>

Sparks, J. O, Lindstrom, R. E. (1971) Separation of Rare Earth Elements by Ion Exchange. U.S. Patent 3,615,173. Washington, DC: US. Retrieved June 19, 2014 from <http://www.google.com/patents/US3615173>

Spedding, F.H., Wheelwright, J., Powell, J.E. (1957) Method of Separating Rare Earths. U.S. Patent 2,798789. Washington, DC: US. Retrieved June 23, 2014 from <http://www.google.com/patents/US2798789>

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**Section III: Document Control Information**

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**Revision History:**

Original/no revisions

**How to Cite This Document:** This document should be cited as:

NETL (2014). NETL Life Cycle Inventory Data – Unit Process: Separation of rare earth elements using ion exchange – Version 01. U.S. Department of Energy, National Energy Technology Laboratory. Retrieved [Date] from [www.netl.doe.gov/LCA](http://www.netl.doe.gov/LCA).

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