NETL Life Cycle Inventory Data
Process Documentation File

Process Name: Rare earth oxide formation

Reference Flow: 1 kg of rare earth chloride hexahydrate

Brief Description: Precipitation of rare earth oxylates from aqueous rare earth chlorides and subsequent calcination to form rare earth oxides

Section I: Meta Data

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:

Ce_out	*[binary] Parameter to select cerium metal as the output*
La_out	*[binary] Parameter to select lanthanum metal as the output*
Pr_out	*[binary] Parameter to select praseodymium metal as the output*

Nd_out	*[binary] Parameter to select neodymium metal as the output*
Sm_out	*[binary] Parameter to select samarium metal as the output*
Eu_out	*[binary] Parameter to select europium metal as the output*
Gd_out	*[binary] Parameter to select gadolinium metal as the output*
Tb_out	*[binary] Parameter to select terbium metal as the output*
Dy_out	*[binary] Parameter to select dysprosium metal as the output*
Ho_out	*[binary] Parameter to select holmium metal as the output*
Er_out	*[binary] Parameter to select erbium metal as the output*
Tm_out	*[binary] Parameter to select thulium metal as the output*
Yb_out	*[binary] Parameter to select ytterbium metal as the output*
Lu_out	*[binary] Parameter to select lutetium metal as the output*
Y_out	*[binary] Parameter to select yttrium metal as the output*
recovery_rate	*[kg/kg] kg of REO produced per kg of REO-equivalent in rare earth chloride*
heat_reqd	*[kJ/kg] kJ of heat required to calcine the rare earth oxalate to rare earth oxide*

Tracked Input Flows:

rare earth chloride hexahydrate	*Reference flow*
heat	*Technosphere*
oxalic acid	*Technosphere*
water	*Resource*

Tracked Output Flows:

rare earth oxide	*Intermediate product*
Carbon dioxide	*Emissions to air*
Hydrochloric acid waste	*Mixed waste*
Water	*Mixed waste*

Section II: Process Description

Associated Documentation

This unit process is composed of this document and the data sheet (DS) *DS_Stage1_O_Rare_earth_oxide_formation_2014.01.xlsx*, which provides additional details regarding relevant calculations, data quality, and references.

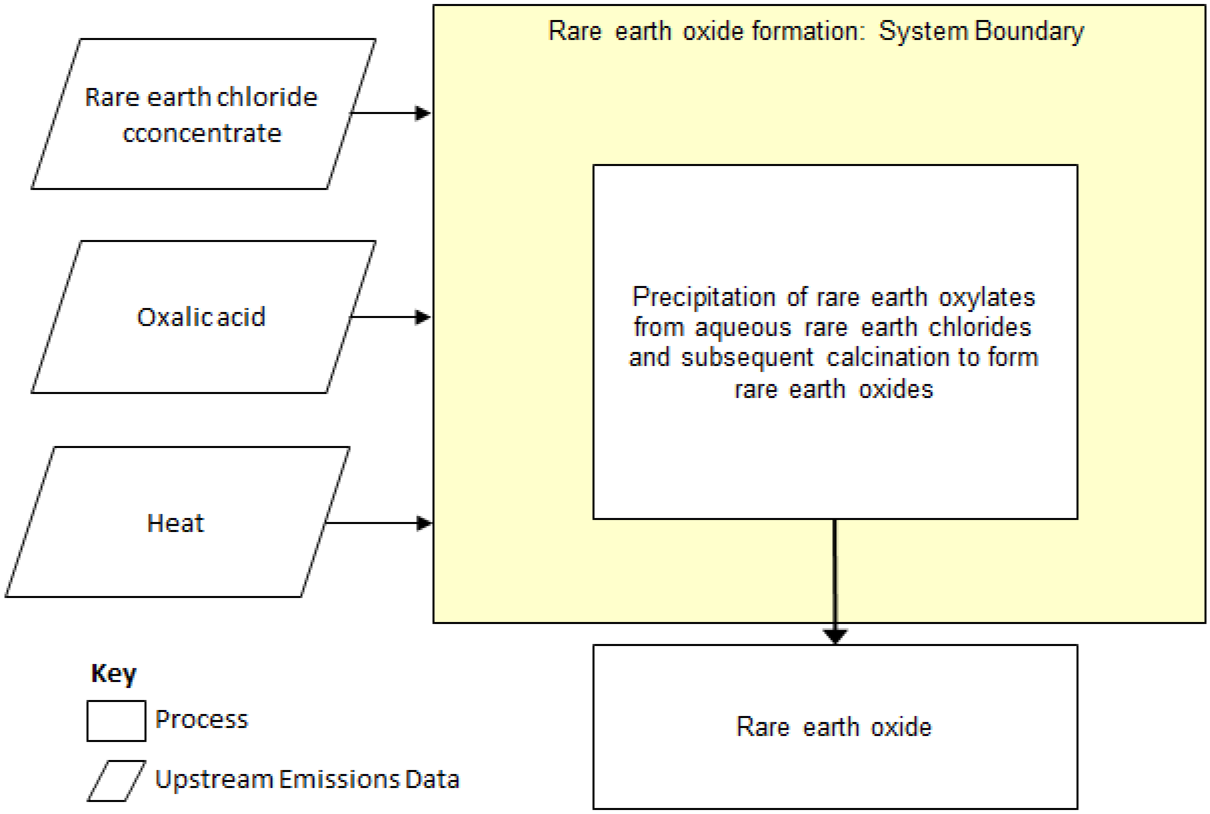
Goal and Scope

This unit process provides a summary of relevant input and output flows associated with the conversion of rare earth chlorides into rare earth oxides. The process involves first converting the rare earth chlorides into rare earth oxalates using oxalic acid and then calcining the oxalate to convert those into rare earth oxides. The reference flow of this unit process is: 1 kg of rare earth chloride hexahydrate.

Boundary and Description

Figure 1 provides an overview of the boundary of this unit process. Rectangular boxes represent relevant sub-processes, while trapezoidal boxes indicate upstream data that are outside of the boundary of this unit process. As shown, the upstream emissions for rare earth chloride concentrate, oxalic acid, and heat are calculated in another unit process. The methods for calculating these operating activities are described below.

Figure 1: Unit Process Scope and Boundary



After the aqueous rare earths have been separated from each other via solvent extraction, the rare earth chlorides are precipitated from the aqueous solution by the addition of oxalic acid (Schüler et al., 2011). Hydrochloric acid is generated as a result of this reaction. After filtering the solid rare earth oxalates from solution, the precipitate is then calcined to remove the carbon and some of the oxygen to create rare earth oxides (Schüler et al., 2011). These rare earth oxides are either finished products or ready for reduction into rare earth metals.

The amount of oxalic acid required to react with the rare earth chlorides is based on the stoichiometric requirements of **Reaction [1]** assuming only 1 kg of incoming rare earth chloride hexahydrate as the reference flow. The reaction produces rare earth oxalate decahydrate and hydrochloric acid.

$$2RECl_3 \cdot 6H_2O + 3H_2C_2O_4 \rightarrow RE_2(C_2O_4)_3 \cdot 10H_2O + 6HCl \quad [1]$$

where, RE is any of the lanthanide rare earth elements.

The rare earth oxalate is then calcined to create rare earth oxides and carbon dioxide, and consequently release the water previously bonded to the oxalate, as shown in **Reactions [2]** through **[5]**, for cerium, praseodymium, terbium, and the rest of the rare earth elements respectively. The equations are modified from the equation provided *Rare earths; the fraternal fifteen* to show the bonded water molecules and account for the different REO (Gschneidner, 1964). The oxygen in the equation is assumed to come from ambient air, so it isn't tracked as an input. Also while the water would be released as steam, it is assumed that the steam is recovered rather than vented.

$$Ce_2(C_2O_4)_3 \cdot 10H_2O + 2O_2 \xrightarrow{heat} 2CeO_2 + 6CO_2 + 10H_2O \quad [2]$$

$$6Pr_2(C_2O_4)_3 \cdot 10H_2O + 11O_2 \xrightarrow{heat} 2Pr_2O_{11} + 36CO_2 + 60H_2O \quad [3]$$

$$4Tb_2(C_2O_4)_3 \cdot 10H_2O + 7O_2 \xrightarrow{heat} 2Tb_4O_7 + 24CO_2 + 40H_2O \quad [4]$$

$$2RE_2(C_2O_4)_3 \cdot 10H_2O + 3O_2 \xrightarrow{heat} 2RE_2O_3 + 12CO_2 + 40H_2O \quad [5]$$

Heat input is estimated based on a calcine temperature of 1000 ºC, which is held for an hour (Smith, 2007). Part of the heat input is the amount required to increase the temperature of the rare earth oxalate (specifically cerium) from 20 ºC to 1000 ºC. The specific heat of cerium oxalate hydrate is estimated using weighted averages of individual element or compound specific heats, also known as Kopp's Law (Hall, 2000). Once the target temperature is reached, the amount of heat lost for the hour calcination time is estimated assuming that the furnace is a cube with edge length of 1 m (an area of 6 m^2) and insulated using low-temperature firebrick. No assumption is made as to the source of heat.

Table 2: Unit Process Input and Output Flows

Flow Name	Ce	La	Pr	Nd	Sm	Eu	Units (Per Reference Flow)
Inputs							
rare earth chloride hexahydrate	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	kg
heat	3.39E+03	3.39E+03	3.39E+03	3.39E+03	3.39E+03	3.39E+03	kJ
oxalic acid	3.81E-01	3.82E-01	3.80E-01	3.77E-01	3.70E-01	3.69E-01	kg
water	1.02E-01	1.02E-01	1.01E-01	1.00E-01	9.88E-02	9.83E-02	kg
Outputs							
rare earth oxide	4.85E-01	4.61E-01	4.79E-01	4.69E-01	4.78E-01	4.80E-01	
Carbon dioxide [Inorganic emissions to air]	3.72E-01	3.74E-01	3.72E-01	3.68E-01	3.62E-01	3.60E-01	kg
Hydrochloric acid waste	3.08E-01	3.10E-01	3.08E-01	3.05E-01	3.00E-01	2.99E-01	kg
Water	2.54E-01	2.55E-01	2.53E-01	2.51E-01	2.47E-01	2.46E-01	kg

Flow Name	Gd	Tb	Dy	Ho	Er	Tm	Units (Per Reference Flow)
Inputs							
rare earth chloride hexahydrate	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	kg
heat	3.39E+03	3.39E+03	3.39E+03	3.39E+03	3.39E+03	3.39E+03	kJ
oxalic acid	3.63E-01	3.62E-01	3.58E-01	3.56E-01	3.54E-01	3.52E-01	kg
water	9.69E-02	9.65E-02	9.56E-02	9.50E-02	9.44E-02	9.40E-02	kg
Outputs							
rare earth oxide	4.88E-01	5.01E-01	4.95E-01	4.98E-01	5.01E-01	5.03E-01	
Carbon dioxide [Inorganic emissions to air]	3.55E-01	3.54E-01	3.50E-01	3.48E-01	3.46E-01	3.44E-01	kg
Hydrochloric acid waste	2.94E-01	2.93E-01	2.90E-01	2.88E-01	2.87E-01	2.85E-01	kg
Water	2.42E-01	4.82E-01	2.39E-01	2.37E-01	2.36E-01	2.35E-01	kg

Flow Name	Yb	Lu	Y	Units (Per Reference Flow)
Inputs				
rare earth chloride hexahydrate	1.00E+00	1.00E+00	1.00E+00	kg
heat	3.39E+03	3.39E+03	3.39E+03	kJ
oxalic acid	3.49E-01	3.47E-01	4.45E-01	kg
water	9.30E-02	9.25E-02	1.19E-01	kg
Outputs				
rare earth oxide	5.08E-01	5.11E-01	3.72E-01	
Carbon dioxide [Inorganic emissions to air]	3.41E-01	3.39E-01	4.35E-01	kg
Hydrochloric acid waste	2.82E-01	2.81E-01	3.61E-01	kg
Water	2.32E-01	2.31E-01	2.97E-01	kg

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

Embedded Unit Processes

None.

References

Schüler, D. et al. (2011). Study on Rare Earths and Their Recycling. Freiburg, Germany: Öko-Institute e.V.

Gschneidner Jr., K.A. (1964). Rare earths; the fraternal fifteen. Washington, D.C.: U.S. Atomic Energy Commission.

Smith, P. M. (2007). High-Purity Rare Earth Oxides Produced via Precipitation Stripping. Metallurgical and Materials Transactions B, 38B.

Hall, C.W. (2000). Laws and Models: Science, Engineering, and Technology. Boca Raton, FL: CRC Press.

Section III: Document Control Information

Date Created: June 17, 2014

Point of Contact: Timothy Skone (NETL), Timothy.Skone@NETL.DOE.GOV

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: Rare earth oxide formation – Version 01. U.S. Department of Energy, National Energy Technology Laboratory. Retrieved [DATE] from www.netl.doe.gov/LCA

Section IV: Disclaimer

Neither the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) nor any person acting on behalf of these organizations:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this document, or that the use of any information, apparatus, method, or process disclosed in this document may not infringe on privately owned rights; or

B. Assumes any liability with this report as to its use, or damages resulting from the use of any information, apparatus, method, or process disclosed in this document.

Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by NETL. The views and opinions of the authors expressed herein do not necessarily state or reflect those of NETL.