NETL Life Cycle Inventory Data
Process Documentation File

Process Name: bastnaesite calcination

Reference Flow: 1 kg of rare earth concentrate

Brief Description: Calcination of bastnaesite with chloride leaching and ceric oxide separation

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: Individual 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:

perc_RE	*[kg/kg] mass rare earth (REO-equivalent) per kg of concentrate input*
RE_bast_conv	*[kg/kg] kg of bastnaesite per kg of REO equivalent (site-specific)*
calc_temp	*[deg C] Temperature of calcination process*
starting_temp	*[deg C] Starting temperature of ore from calcination or comminution*

time_for_leach	*[hrs] Time for calcination*
U_ins	*[J/s-m^2-K] Heat transfer coefficienct (used to estimate heat loss), default assumes 6-inch thick firebrick*
perc_Ce	*[kg/kg] kg of elemental cerium per kg of bastnaesite*
perc_noCe	*[kg/kg] kg of elemental rare earths minus cerium per kg of bastnaesite*
molwt_noCE	*[kg/mol] kg elemental rare earths minus cerium per mol of mixture minus cerium*

Tracked Input Flows:

rare earth ore concentrate [Valuable substances]	*Reference flow - ore input for the leaching process (from beneficiation)*
hydrochloric acid (100%)	*[Technosphere] Hydrochloric acid*
caustic soda	*[Technosphere] Caustic soda*
Heat input	*[Technosphere] From CHP facility*

Tracked Output Flows:

rare earth chlorides [Intermediate products]	*Intermediate product*
Sodium Fluoride [Intermediate products]	*Intermediate product*
Ceric oxide	*Final product*
solid waste	*Solid waste to on-site storage*
waste water, leaching and calcination	*Intermediate product*

Section II: Process Description

Associated Documentation

This unit process is composed of this document and the data sheet (DS) *DS_Stage1_O_Bastnaesite_Calcination_2014.01.xlsx*, which provides additional details regarding relevant calculations, data quality, and references.

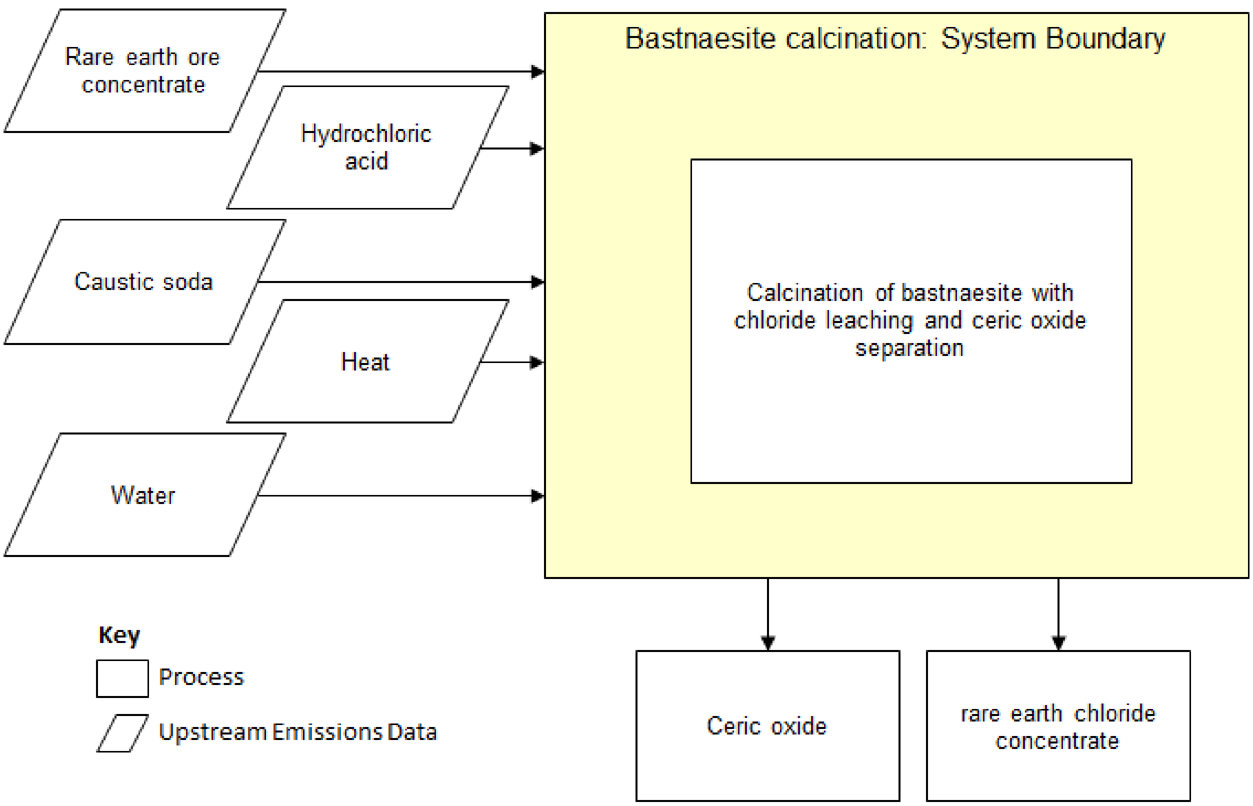
Goal and Scope

This unit process provides a summary of relevant input and output flows associated with the calcination and acid leaching of bastnaesite, producing a mix of cerium oxides, rare earth chlorides and hydroxides. The products are assumed to be precipitated (as applicable), dried, and filtered providing solid and liquid waste flows. The reference flow of this unit process is: 1 kg of rare earth concentrate.

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 from natural or associated gas and water are calculated in another unit process. The methods for calculating these operating activities are described below.

Figure 1: Unit Process Scope and Boundary



Calcination is a thermal process that is used here to remove carbon dioxide from the rare earth mineral bastnaesite (composition detailed in **Table 1**), thus increasing the total concentration of rare earth oxides. During the process, cerium is oxidized to Ce(+4) and forms solid ceric oxide (CeO_2), a finished rare earth product, **Equation [1]** (Pradip et al., 2013). The fluorine in the ceric oxide reaction is modeled as released to atmosphere because specific information on whether fluorine gas is captured could not be found in the literature. The rest of the rare earths in the bastnaesite take the form of rare earth oxygen fluorides (REFO), **Equation [1]** (Chi et al. 2006). The mix of ceric oxide and rare earth oxygen fluorides are leached with hydrochloric acid (Gupta & Krishnamurthy, 2005). The stable ceric oxide remains a solid while the other rare earths form either aqueous rare earth chlorides ($RECl_3$) or solid rare earth fluorides (REF_3) in the ratio of 2 $RECl_3$ to 1 REF_3, **Equations [2]** and **[3]** (Gupta & Krishnamurthy). The solid rare earth fluorides and ceric oxide are separated from the aqueous rare earth chlorides, which is then dried, forming $RECl_3$-hydrates ($RECl_3 \cdot 6H_2O$) to be sent for further processing (Gupta & Krishnamurthy).

The solid ceric oxides and rare earth fluorides are separated by reaction with caustic soda to form aqueous rare earth hydroxides and solid ceric oxides (Gupta & Krishnamurthy, 2005). The ceric oxide solids are filtered and removed as a finished product (Gupta & Krishnamurthy). The rare earth hydroxides are combined with hydrochloric acid to create more rare earth chlorides, **Equation [4]** (Gupta & Krishnamurthy).

The stoichiometry for the reactions is sensitive to the parameters *perc_RE* and *RE_bast_conv*, which are the percent REO contained in the incoming rare earth concentrate and the conversion factor for REO to bastnaesite. The conversion is shown in **Table 1** for Mountain Pass bastnaesite (Gupta & Krishnamurthy, 2005). The maximum value for *perc_RE* is the value at which the incoming rare earth concentrate is 100 percent bastnaesite. Anything less than that value is assumed to result in solid waste being generated as gangue material.

$$2\mathrm{CeFCO_3} + \mathrm{O_2} \rightarrow 2\mathrm{CeO_2} + 2\mathrm{CO_2} + \mathrm{F_2} \quad [1]$$

$$\mathrm{REFCO_3} \rightarrow \mathrm{REFO} + \mathrm{CO_2}$$

Where RE represents all rare earth elements other than cerium (La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, and Sc)

$$3\mathrm{REFO} + 9\mathrm{HCl} \rightarrow \mathrm{REF_3} + 2\mathrm{RECl_3} + 3\mathrm{H_2O} + 3\mathrm{HCl} \quad [2]$$

$$\mathrm{CeO_2} + \mathrm{REF_3} + 3\mathrm{NaOH} \rightarrow \mathrm{RE(OH)_3} + 3\mathrm{NaF} + \mathrm{CeO_2} \quad [3]$$

$$\mathrm{RE(OH)_3} + 3\mathrm{HCl} \rightarrow \mathrm{RECl_3} + 6\mathrm{H_2O} \quad [4]$$

The calcining process occurs at 620ºC for 4 hours (Gupta & Krishnamurthy, 2005). Rather than assume a specific type of heat generation including efficiencies, this unit process estimates the heat required to raise the bastnaesite temperature from 20ºC to 620ºC, **Equation [5]**. The specific heat of the bastnaesite is estimated using Kopp's Law for cerium-bastnaesite only since it constitutes the majority of Mountain Pass bastnaesite (Hall, 2000 and Gupta & Krishnamurthy). Heat loss is estimated assuming that the calcination reactor is lined with 0.1524-m (6-inch) firebrick for insulation with a total of surface area of 6 m^2 (a cube with edge length of 1 meter), **Equation [6]** (DOE, 2009). Insulation values are provided for 3-inch and 12-inch thick firebrick to provide a range of uncertainty.

$$Q_h = \mathrm{c_p} \frac{\mathrm{J}}{\mathrm{g \cdot \Delta K}} \cdot (\mathrm{T_f} - \mathrm{T_i})\ \mathrm{K} \cdot 1\ \mathrm{kg} \cdot \frac{1000\ \mathrm{g}}{\mathrm{kg}} \cdot \frac{1\ \mathrm{kJ}}{1000\ \mathrm{J}} \qquad [5]$$

where,

Q_h is the heat required to heat the bastnaesite to calcination temperature (kJ)

c_p is the specific heat of water (0.4098 J/g-K)

T_f is the final temperature (620ºC)

T_i is the initial temperature (20ºC)

$$\mathrm{Q_l} = \mathrm{U_{ins}} \frac{\mathrm{J}}{\mathrm{hr \cdot m^2 \cdot \Delta K}} \cdot \mathrm{A\ m^2} \cdot \mathrm{t\ hr} \cdot (\mathrm{T_{reactor}} - \mathrm{T_{amb}})\ \mathrm{K} \cdot \frac{\mathrm{kJ}}{1000\ \mathrm{J}} \qquad [6]$$

where,

Q_l is the heat loss during calcination (kJ)

U_{ins} is the heat transfer coefficient (5.7686 J/hr-m^2-ΔK)

$T_{reactor}$ is the temperature inside the reactor (620ºC)

T_{amb} is the ambient temperature (20ºC)

A is the surface area of the reactor (6 m^2)

t is the time for calcination (4 hrs)

Table 1: Typical Makeup of Bastnaesite from Mountain Pass Rare Earths Mine

Rare Earth Oxide	Fraction of Bastnaesite Rare Earth Oxide Content (kg/kg TREO)	Bastnaesite Component	Fraction of bastnaesite (kg bastnaesite/kg TREO)
CeO_2	4.81E-01	$CeFCO_3$	6.25E-01
La_2O_3	3.41E-01	$LaFCO_3$	4.44E-01
Pr_6O_{11}	4.31E-02	$PrFCO_3$	5.61E-02
Nd_2O_3	1.22E-01	$NdFCO_3$	1.59E-01
Sm_2O_3	7.98E-03	$SmFCO_3$	1.04E-02
Eu_2O_3	1.19E-03	$EuFCO_3$	1.55E-03
Gd_2O_3	1.66E-03	$GdFCO_3$	2.16E-03
Tb_4O_7	1.56E-04	$TbFCO_3$	2.02E-04
Dy_2O_3	3.11E-04	$DyFCO_3$	4.04E-04
Ho_2O_3	5.06E-05	$HoFCO_3$	6.58E-05
Er_2O_3	3.46E-05	$ErFCO_3$	4.51E-05
Tm_2O_3	8.89E-06	$TmFCO_3$	1.16E-05
Yb_2O_3	5.90E-06	$YbFCO_3$	7.68E-06
Lu_2O_3	9.81E-07	$LuFCO_3$	1.28E-06
Y_2O_3	1.04E-03	$YFCO_3$	1.36E-03
Total	1.0000	Total	1.30E+00

Water demand is modeled only as a function of diluting 100 percent hydrochloric acid to 30 percent strength (Gupta & Krishnamurthy, 2005). There is a greater amount of water discharged than demanded because of the water coming out of the chlorination reaction (Gupta & Krishnamurthy).

Table 2: Unit Process Input and Output Flows

Flow Name	Value	Units (Per Reference Flow)
Inputs		
Rare earth ore concentrate [Valuable substances]	1.00E+00	kg
Hydrochloric acid (100%)	3.23E-01	kg
Caustic soda	8.87E-02	kg
Heat input	3.29E+02	kJ
Water	7.54E-01	kg
Outputs		
Rare earth chlorides [Intermediate products]	7.87E-01	kg
Carbon dioxide [Inorganic emissions to air]	1.88E-01	kg
Sodium Fluoride [Intermediate products]	9.31E-02	kg
Ceric oxide	3.54E-01	kg
Fluorine [Inorganic emissions to air]	3.90E-02	kg
Solid waste	6.35E-02	kg
Waste water, leaching and calcination	7.15E-01	kg

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

Embedded Unit Processes

None.

References

Chi, R., Li, Z., Peng, C., Gao, H., & Xu, Z. (2006). Preparation of Enriched Cerium Oxide from Bastnasite with Hydrochloric Acid by Two-Step Leaching. Mettalurgical and Materials Transactions B. Springer US.

DOE (2009). Maximize System Efficiency with Proper Insulation. Energy Matters, Winter 2009. Retrieved 3/3/2014 from http://www1.eere.energy.gov/manufacturing/tech_assistance/winter2009.html

Gupta, C.K. and Krishnamurthy, N. (2005). Extractive Metallurgy of Rare Eaths. Boca Raton, FL: CRC Press.

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

Pradip, C. & Fuerstenau, W. (2013). The Snythesis and Characterization of Rare-Earth Fluocarbonates. *KONA Powder and Particle Journal No. 30*. Hosokawa Powder Technology Foundation.

Section III: Document Control Information

Date Created: March 5, 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: bastnaesite calcination – Version 01. U.S. Department of Energy, National Energy Technology Laboratory. Retrieved [DATE] from http://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.