NETL Life Cycle Inventory Data
Process Documentation File

Process Name: Metallothermic Reduction of Rare Earth Oxides

Reference Flow: 1 kg of rare earth metal

Brief Description: Metallothermic reduction of a rare earth oxide through calcium chloride and sodium.

Section I: Meta Data

Geographical Coverage: United States **Region:** N/A

Year Data Best Represents: 2013

Process Type: Basic Process (BP)

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:

Na_mass_in	*[kg/kg] kg of sodium per kg of concentrate input*
CaCl2_in	*[kg/kg] kg of calcium chloride per kg of concentrate input*
CaO_out	*[kg/kg] kg of calcium oxide per kg of concentrate created*
NaCl_out	*[kg/kg] kg of sodium chloride per kg of concentrate created*

recovery_rate	*[kg/kg] kg of rare earth metal recovered per rare earth oxide input*
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*

Tracked Input Flows:

Electricity	*[Technosphere] Energy*

Rare Earth Oxide	*[Technosphere] Rare earth oxide*
Sodium	*[Technosphere] Sodium*
Calcium Chloride	*[Technosphere] Calcium Chloride*

Tracked Output Flows:

Rare Earth Metal	*Reference Flow*
Sodium Chloride	*Emission to Water*
Calcium Oxide	*Emission to Water*

Section II: Process Description

Associated Documentation

This unit process is composed of this document and the data sheet (DS) *DS_Stage1_O_Metallothermic_Red_REO_2014_01.xlsx*, which provides additional details regarding relevant calculations, data quality, and references.

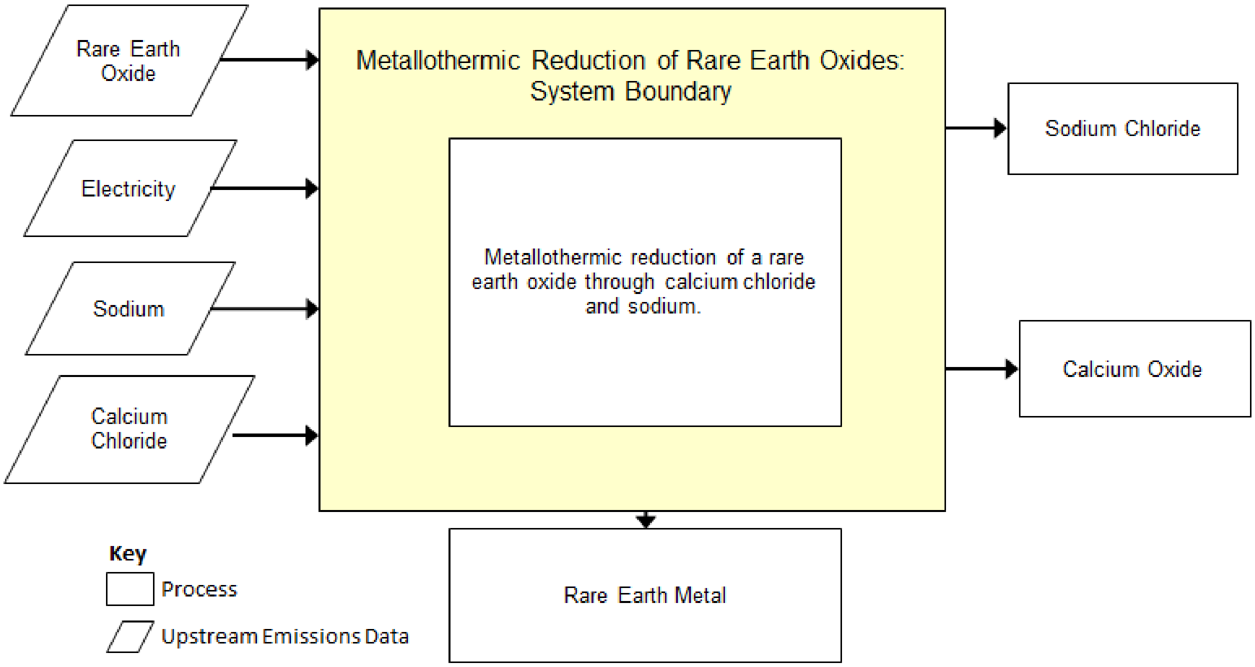
Goal and Scope

This unit process provides a summary of relevant input and output flows associated with metallothermic reduction of a rare earth oxide (REO) to rare earth (RE) metal. The process uses platinum wares and a tantalum crucible in high temperatures (above 1800 degrees Celsius). Inputs include process heat, sodium, and calcium chloride. The output is a solid RE metal, sodium chloride (salt), and calcium oxide. The reference flow of this unit process is: 1 kg of RE metal.

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 REO, electricity, sodium, and calcium chloride are calculated from other unit processes. The methods for calculating these operating activities are described below.

Figure 1: Unit Process Scope and Boundary



Metallothermic reactions are concerned with the preparation of metals and alloys by reduction of their oxides or halides with a metal (EPA, 2012). These reactions can be expressed in general by the equation: AX + B → A + BX, where X is oxygen, chlorine, or fluorine, and A and B are two metals. Characterized by the fact that the reducing metal is converted to either a solid or a liquid product, and not to a gas as in other reduction processes (e.g., by carbon or hydrogen where CO + CO2 and H2O are formed, respectively). This method is used when reduction by carbon and hydrogen or by electrowinning from aqueous solutions is not possible (EPA, 2012).

One of the standard procedures to obtain rare earth metals (REMs) from rare earth oxides (REOs) is through metallothermic reduction using calcium chloride ($CaCl_2$) and sodium (EPA, 2012). The REOs are dispersed in a molten bath along with sodium metal (Na). The sodium reacts with the calcium chloride to produce calcium metal which reduces the REOs to REMs. The REMs are collected in a discrete layer in the reaction vessel (Gupta & Krishnamurthy, 2005).

In 1987, Sharma patented the metallothermic reduction of REOs using calcium chloride bath and sodium metal (Sharma, 1987). The procedure occurs in a helium atmosphere (<1 parts per million [ppm] O_2, N_2 or H_2O) dry box that has a 130 millimeter (mm) diameter by 550 mm depth furnace extending beneath its floor. The reduction reaction occurs in a tantalum crucible, 100 mm diameter by 130 mm depth with a 1.5 mm thick wall (Sharma, 1987).

To run the reaction, the vessel is heated to a temperature above the melting point of the constituents (about 675 ºC) but below the vaporization temperature of sodium metal (about 900 ºC in RE reduction reactions) (Sharma, 1987). REM melting point and vaporization temperatures were obtained from Piero & Menendez (2013). The molten constituents are rapidly stirred in the vessel to keep them in contact with one another as the reaction progresses. The $CaCl_2$ acts as a source of calcium metal to reduce REO and triggers the reduction reaction to produce the REM (Gupta & Krishnamurthy, 2005).

Several different and competing chemical reactions occur in the vessel; however the reduction of the REO is accomplished in accordance with **Reaction [1]** (Sharma, 1987).

$$RE_nO_m + mCa \rightarrow mCaO + nRE \quad [1]$$

where,
n and *m* are the number of moles of constituent and where the relation of n and m is determined by the oxidation state of the RE element
RE represents all rare earth elements (Ce, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, and Sc)
The composite **Reaction [2]** is:

$$RE_nO_m, + m\ CaCl_2 + 2m\ Na \rightarrow n\ RE + mCaO + 2mNaCl \quad [2]$$

For example, the reduction of neodymium oxide (Nd_2O_3) would be **Reaction [3]** :

$$Nd_2O_3 + 3CaCl_2 + 6Na \rightarrow 2Nd + 3CaO + 6NaCl \quad [3]$$

When stirring is stopped, the reduced REM is recovered in a clean layer at the bottom of the reaction vessel. This layer may be tapped while molten or separated from the salt layer after it solidifies (Sharma, 1987).

The default recovery rate (0.90 kg of REM product per kg of REO input) is applied to all of the different rare earths and is based on the minimum recovery rate listed in the Sharma metallothermic reduction of REO patent (Sharma, 1987).

Table 1 shows the energy and material requirements for the different REMs.

Table 1: Unit Process Input and Output Flows

Flow Name (Units)	CeO_2	La_2O_3	Pr_6O_{11}	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3	Tb_4O_7	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3	Y_2O_3	Units (Per Ref. Flow)
Inputs																
Electricity	9.17E-02	1.06E-01	1.11E-01	1.17E-01	1.31E-01	1.17E-01	1.61E-01	1.50E-01	1.56E-01	1.58E-01	2.22E-01	1.94E-01	9.17E-02	2.06E-01	2.86E-01	kWh
REO	1.36E+00	1.30E+00	1.34E+00	1.30E+00	1.29E+00	1.29E+00	1.28E+00	1.31E+00	1.28E+00	1.27E+00	1.27E+00	1.27E+00	1.27E+00	1.26E+00	1.41E+00	kg
Sodium	7.30E-01	5.52E-01	6.65E-01	5.31E-01	5.10E-01	5.04E-01	4.88E-01	5.63E-01	4.72E-01	4.65E-01	4.58E-01	4.54E-01	4.43E-01	4.38E-01	8.62E-01	kg
Calcium Chloride	1.76E+00	1.33E+00	1.60E+00	1.28E+00	1.23E+00	1.22E+00	1.18E+00	1.36E+00	1.14E+00	1.12E+00	1.11E+00	1.09E+00	1.07E+00	1.06E+00	2.08E+00	kg
Outputs																
REM	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	kg
Sodium Chloride	1.85E+00	1.40E+00	1.69E+00	1.35E+00	1.30E+00	1.28E+00	1.24E+00	1.43E+00	1.20E+00	1.18E+00	1.16E+00	1.15E+00	1.13E+00	1.11E+00	2.19E+00	kg
Calcium Oxide	8.89E-01	6.73E-01	8.11E-01	6.48E-01	6.22E-01	6.15E-01	5.94E-01	6.86E-01	5.75E-01	5.67E-01	5.59E-01	5.53E-01	5.40E-01	5.34E-01	1.05E+00	kg

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

Embedded Unit Processes

None.

References

EPA. (2013). Rare Earth Elements: A Review of Production, Processing, Recycling, and Associated Environmental Issues. U.S. Environmental Protection Agency Office of Research and Development: Cincinnati. EPA 600/R-12/572. Retrieved May 9, 2014 from http://nepis.epa.gov/Adobe/PDF/P100EUBC.pdf.

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Piero, L., Menendez, G. (2013). Material and Energy Requirement for Rare Earth Production. Journal of The Minerals, Metals & Materials Society, 65(10), pp 1327-1340. Accessed June 6 from http://download.springer.com/static/pdf/302/art%253A10.1007%252Fs11837-013-0719-8.pdf?auth66=1402756605_08c22ac3cb699ef813c16b06a856a0d7&ext=.pdf

Sharma, Ram A. (1986) Metallothermic Reduction of Rare Earth Oxides. U.S. Patent 4,578,242. Washington, DC: US. Retrieved June 3, 2014 from http://www.google.com/patents/US4578242.

Section III: Document Control Information

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