Calciothermic Reduction for Neodymium Production

A Major Qualifying Project submitted to the faculty of Worcester Polytechnic Institute
in partial fulfillment of the requirements for the degree of Bachelor of Science by:

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Sponsor: Critical Material Institute in collaboration with Terves and Ames Laboratory

Abstract

Rare Earth elements are essential for the production of magnets, electronics, optical and laser materials. These materials are not only found in everyday product but are strategically important for the US government defense system. One of the most important of these elements is neodymium, which has been used as a key component in a widespread of applications. Commercial grade purity neodymium is produced by three main methods; electrolysis using fluoride salts, electrolysis using chloride salts, and calciothermic reduction. In this project, Terves LLC, in collaboration with WPI and Ames Laboratory focuses on developing a semi-continuous process capable of producing 99.9% purity neodymium. The process starts by converting neodymium oxide into neodymium chloride followed by calciothermic reduction in magnesium to produce a master alloy at 700°C. The alloy is purified through vacuum distillation to produce pure neodymium. The thermodynamic modeling for the calciothermic reduction was the main focus for the WPI, while the Terves team was responsible for carrying out the experiments and potential scaling up process. Ames Laboratory has been doing the purification and characterization of the master alloy obtained from Terves' experiments. Initial experiments have yielded 60 wt% of the desired purity of neodymium.

Acknowledge

I would like to extend my appreciation to my advisor and co-advisor respectively from Worcester Polytechnic Institute, Professor Adam Powell and Professor Drew Brodeur. Throughout the project both Adam and Drew were very supportive and passionate about the subject matter at hand. Their suggestions helped guide the entire project as a whole and in turn produced a successful process for the project's sponsors. I am grateful that this Major Qualifying Project (MQP) was able to not only contribute to a cost effective and patented process, but also bringing back production capabilities to the U.S.A. for essential materials.

Furthermore, I would like to genuinely thank Ph.D. candidate Chinenye Chinwego for all her contribution to the project. Chinenye has taken the time to educate me on the subject matter at hand and informed me of how to use FactSage. Thank you to the Terves team, Nicholas Farkas, Andrew Sherman, Jamel Richmond, and Corey Leeson for working with us on a regular cadence. The team provided us with updates on our hypothesis and in turn we improved our model each week based on their results.

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1 Introduction

Rare Earth Elements (REEs) can be defined as the fifteen lanthanides in addition to Scandium and Yttrium in the periodic table as seen in Figure 1. Rare Earth Elements are valuable materials in a wide range of products ranging from consumer goods such as a phone to government defense systems such as Tomahawk missiles[1]. This high demand for REEs has forced governments and private companies into competition for REEs supplies. Despite the name Rare Earth elements, these Elements are readily found across the globe. The cost of processing these elements is one of the reasons more countries are not producing REEs. Therefore, the production of REEs has mainly been done in China for the past two decades. China has been the world supplier for REEs and technically has a monopoly on the industry. All developed nations that need REEs are dependent on China to provide them.

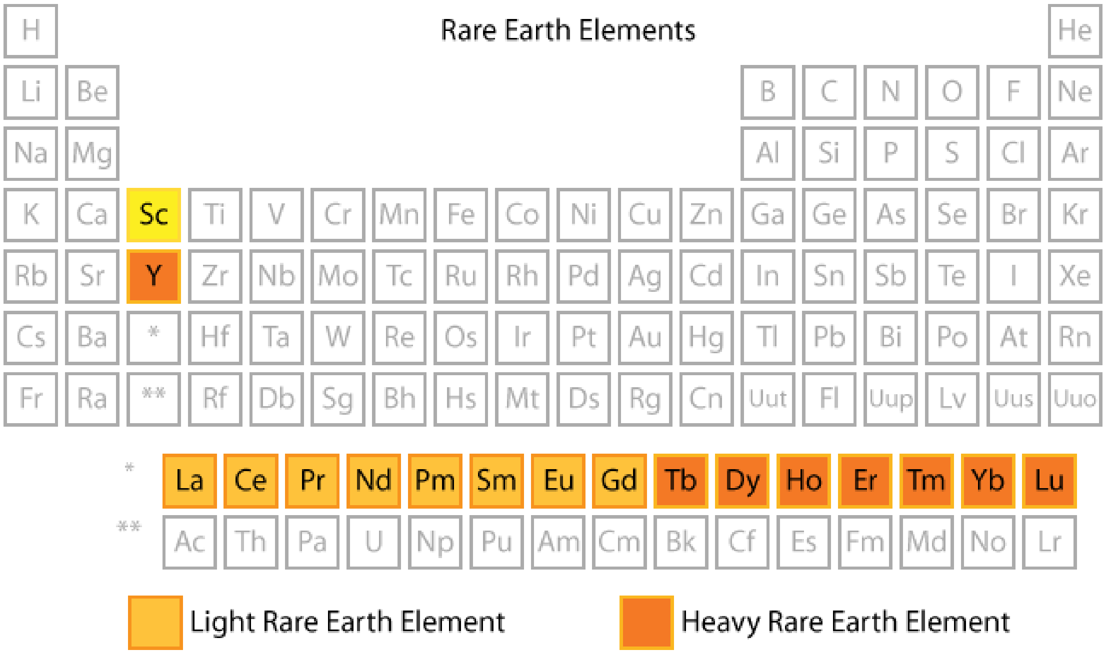


Figure 1:Rare Earth Element Periodic Table [x]

The REEs the United States needed for the Department of Defense (DOD) and American private companies were severely disrupted due to Covid-19. Towards the end of 2019, the Covid-19 virus broke out in China and quickly spread across the globe. China took some drastic measures to contain the spread of the virus by instilling some extreme lockdown procedures across the infected areas and eventually across the country. As the virus spread across the globe, other nations took similar measures to contain the spread of the virus in their respective countries. The global lockdown, in turn, causes a major disruption in the world supply chain. Governments and private entities worked collaboratively in order to make the national supply chain stay afloat while working on a plan to get international trade back to normal.

To combat the supply chain issue for current situations and future disruptions, governments across the globe have been finding ways to produce or diversify their sourcing of REEs. In the United States, the government launches various programs and grants to incentivize companies to find alternate sources for the production of REEs nationally. The previous administration issued Executive Order 13817 directing the government to adopt a strategy that produced critical materials domestically. The Executive Order is to ensure that the Federal Government reduces the Nation's vulnerability to disruptions in the supply of critical minerals, which constitutes a strategic vulnerability for the security and prosperity of the United States [4]. The current administration also takes this issue very seriously as REEs are crucial to national defense and manufacturing. Subsequently, the Department of Defense has offered millions of grant dollars in an effort to help bring back the processing of REEs to the United States. The Department of Energy is funding research to make separating rare earth easier and more efficient and to promote recycling. Its office of Basic Energy Sciences is adding five new national laboratory-led projects focusing on separation science totaling $6.7 million per year. The DOE is investing $25 million per year in the Critical Materials Institute, focusing on securing supply chains for critical materials, strongly centered around rare earth elements and lithium. BES is also announcing $10 million per year in grants for basic research beginning this summer [2]. Universities, laboratories and private companies collaborate to meet the demands for the rare earth elements domestic needs.

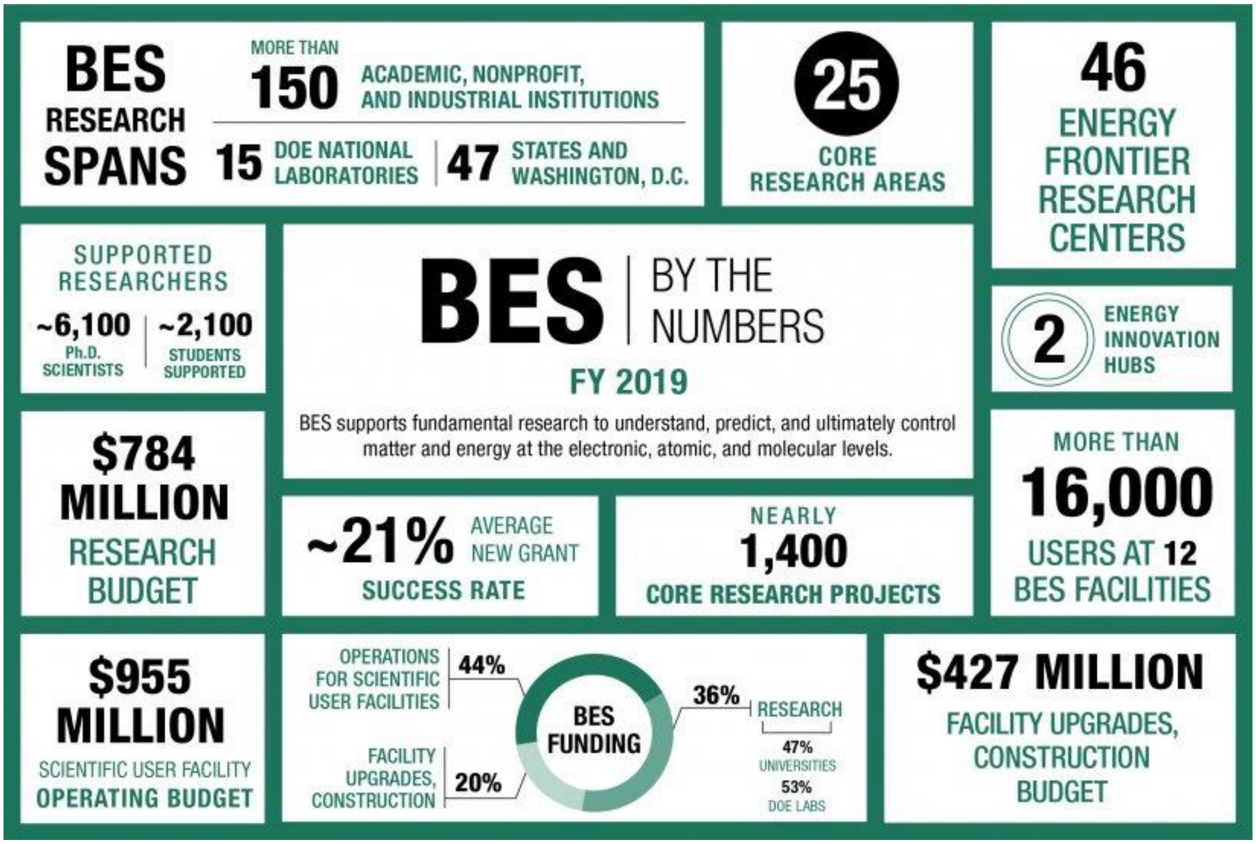


Figure 2: Basic Science Energy Mission that highlight major focus areas and spending categories (Credit to Department of Energy [2])

Terves LLC, in collaboration with WPI, Ames Laboratory, and Powdermet Inc., are working to develop and build a semi-continuous process capable of producing 99.9% purity neodymium (Nd) by converting neodymium oxide (Nd_2O_3) into a neodymium chloride ($NdCl_3$), followed by calciothermic reduction to produce master alloys that can be used in the production of rare earth magnesium alloys and magnets. The primary project goals are to demonstrate the production and handling of mixed salts containing $NdCl_3$, defining the heat, mass and energy balances, overall operation, gain experience on materials compatibility, safety, and operation of a rare earth master alloy production operation.

The proposed processing route is calciothermic reduction from $NdCl_3$ in eutectic molten salts. Commercial purity Nd_2O_3 will be the starting source with calcium metal being used as the reductant in molten chloride salts. $NdCl_3$ will be produced by vacuum reaction with ammonium chloride (NH_4Cl). For handling, the rare earth chloride will be melted into a eutectic salt mixture of NaCl-KCl and then cast into ingots for direct furnace charging. By reducing surface area and diluting the $NdCl_3$, moisture issues will be minimized.

The baseline processing sequence will control the reaction by charging with the initial mixed chloride salt, heating to 700-800°C, and then adding calcium reductant plus iron or magnesium eutectic formers. Using molten metal pumps in a stirring mode, the process is run in semi-batch mode, adding Ca plus eutectic former (Mg or Fe) in a near continuous fashion until reaching roughly 120% of the chloride charge. After settling, the pump is used to remove ingots of metal, and the process is repeated. Adding pure $NdCl_3$ or rich eutectic salt while the furnace is still charged will enable the process to continue until the salt must be lowered or removed, thus itis semi-continuous.

The key deliverables from WPI for this project is thermodynamic models for:

1. Calciothermic Reduction in Calcium
2. Calciothermic Reduction in Magnesium
3. Calciothermic Reduction in Zinc
4. Ternary diagrams for each system
5. Most efficient and cost-effective process recommendation base on thermodynamic modeling

Base on the thermodynamic modeling, WPI can recommend the best process to achieve 99.9% purity neodymium while protecting the environment by minimizing production of greenhouse gasses.

2 Background

Rare Earth Elements have been very important and made technological advancements possible. As the world recognized the importance of REEs, the production of REEs was more balanced across the globe. The breakdown of REEs production in the early 1990s was as follows; 38% of world production of REEs was in China, 33% was in the United States, 12% was in Australia, and 5% each was in Malaysia and India. Several other countries, including Brazil, Canada, South Africa, Sri Lanka, and Thailand, made up the remainder [3]. This balance across the world allowed the supply chain of REEs to withstand any major disruption. However, in the mid-2000s this balance started to shift and by 2008 China accounted for more than 90% of world production of REEs, and by 2011, China accounted for 97% of world production [2]. The dominance of REEs being produced in China caused global issues as China put restrictions on how much REEs can be produced and exported.

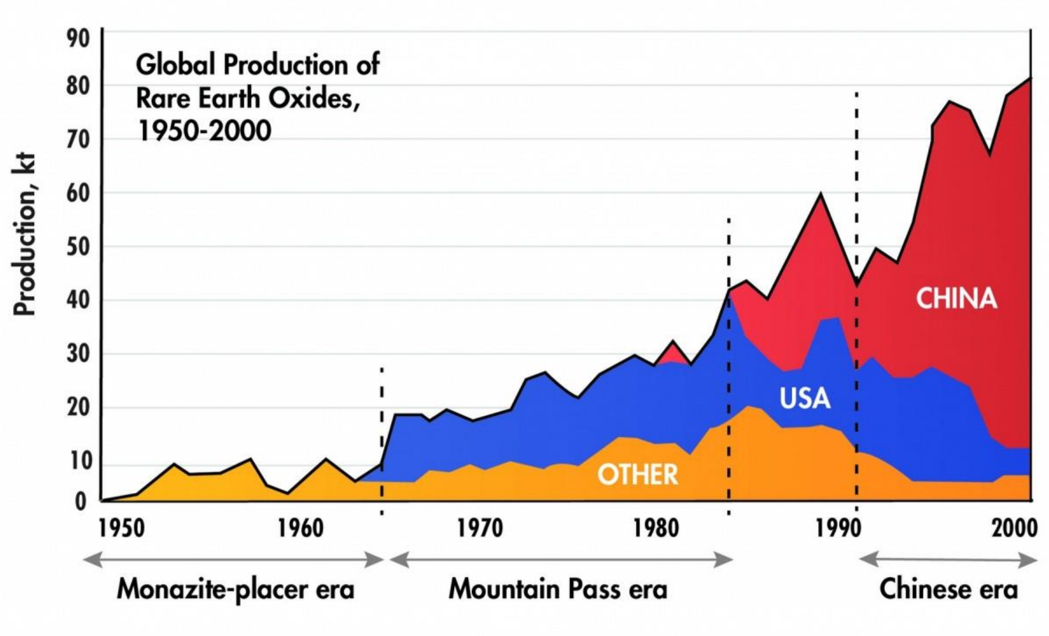


Figure 3:Global Rare Earth Production 1950-2000 (Credit to US Army [2])

Being the top supplier of REEs to the rest of the world allows China to use that market position as a political and diplomatic weapon. China is able to reward those who are politically and strategically aligned with them and punish those who are not. For example, China halted REE shipments to Japan in 2010 as a pressure point to force the Japanese government to release a detained Chinese fishing boat captain. The captain's boat had collided with Japanese Coast Guard ships that were stationed in the water. However, this major water space is controlled by Japan but China claims that water space belongs to them. This dispute over the water space has caused tension between the two governments and the boat incident escalated the issue to the point where China stopped all REE shipments to Japan. Although Japan complied with China’s demands, they did not receive their shipments until two months later. During that two months period, China resumed and blocked the shipments several times as diplomatic negotiation between the two nations failed. After this incident, the US opened an investigation on China to see whether they violated international trade laws for their action against Japan. China then halted REE shipments to the US as retaliation for the investigation. After this dispute, the global production shifted as seen in Figure 4, however, China is still the leader in REE production.

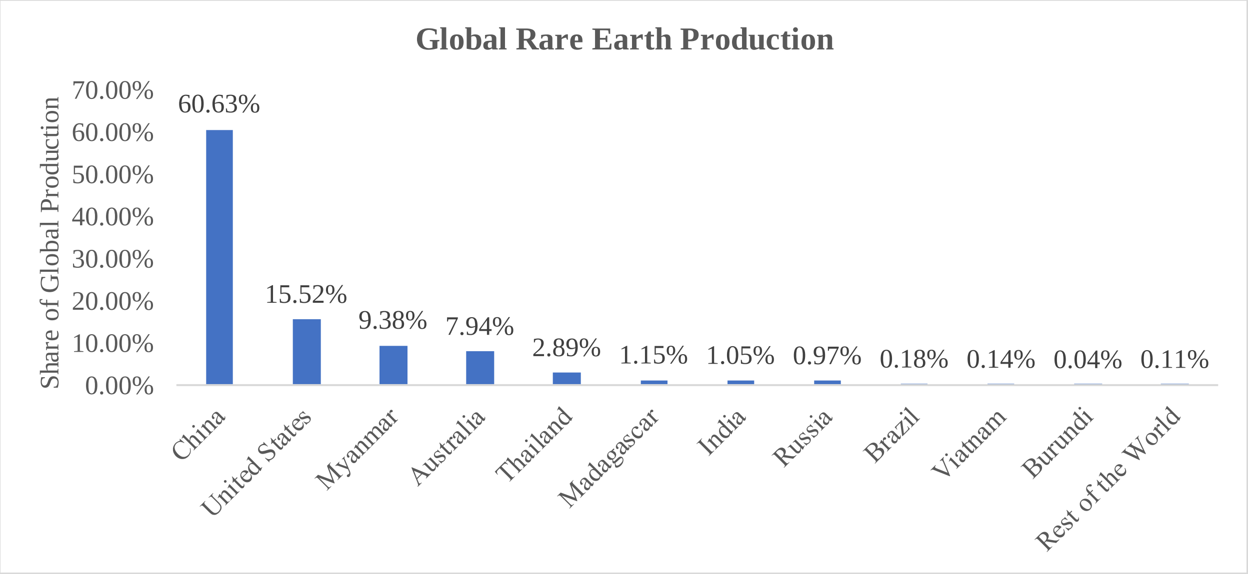


Figure 4:Global Rare Earth Production in 2021(Data is from [1])

Following these incidents and disputes, Congress enacted a few bills and regulations to incentivize the production of REEs in America. Many companies in the industry that were previously shutdown returned to business due to the move by the government. There are also some new players coming into the space, such as Terves and U.S.A Rare Earth.

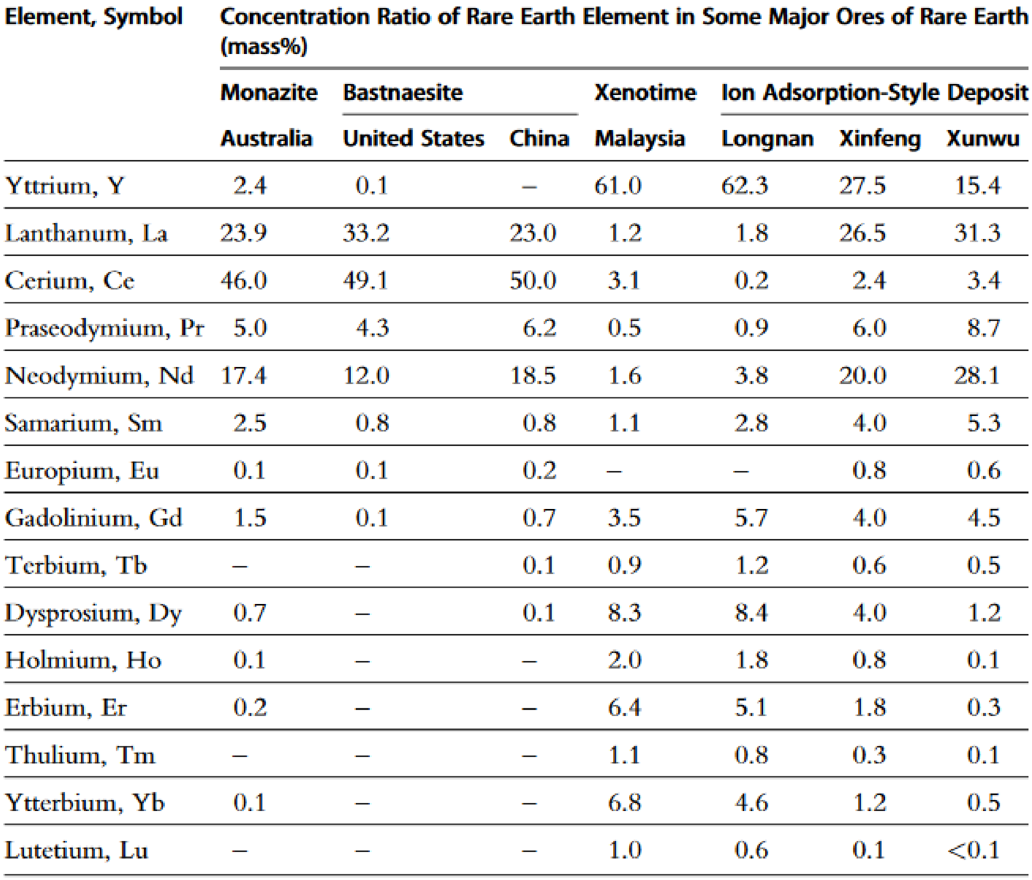
Terves Inc. was formed in July 2013 to raise investment and build a management team focused on commercializing “Engineered Response” materials, initially into oil and gas upstream markets. Terves renovated and opened an 8,400 sq. ft. magnesium foundry capable of producing over 1,000 tons/year of permanent mold ingot castings. Sister company Powdermet Inc. has developed novel materials and material processes to create unique materials, with extensive experience and expertise in the creation of halides for use in chemical vapor deposition coating processes. Terves, with support from Powdermet, Worcester Polytechnic Institute, and Ames Laboratory propose to adapt existing magnesium production infrastructure to the production of rare earth master alloys and pure REEs. Terves infrastructure consists of five 500-3,000-pound magnesium capacity primary melting furnaces, all with controlled atmosphere capability, as well as a holding furnace, low pressure die casting machine, a 60-pound development furnace, and several benchtop casting units for alloy and process development. Terves is one of just two North American producers of magnesium billets and wrought magnesium products, whose primary market is a family of patented dissolvable magnesium alloys (TervAlloy™) and tools used in oil and gas completion operations. After surviving two cycles in the oil and gas industry, building the foundry and extrusion facility, Terves is diversifying into additional markets, including automotive and aerospace, and desires to leverage existing and installed infrastructure to the production of rare earth metals and alloys.

In the next section, the different methods of producing rare earth (neodymium) master alloys will be analyzed based on literature. The advantages and disadvantages for the novel calciothermic reduction process will be explored through the available literature.

3 Literature Review

The literature review will first give a high-level overview of the upstream process consisting of mining the Ores of Rare Earth. Then, explain midstream processes that follow to obtained rare earth chloride, fluoride, and oxide which are used in downstream processes to produce rare earth metal. The main focus in this section is on the downstream processes; electrolysis using fluoride salts, electrolysis using chloride salts, and calciothermic reduction for producing rare earth metals from the midstream products.

To obtain the starting material of neodymium chloride, there are many upstream processes that take place. Ores of REEs must be mined from sites that contain valuable minerals. All the major minerals, monazite and bastnaesite contain an abundance of light and middle rare earths, while xenotime is a rich source of heavy earths [5]. There are some major Ores of Rare Earth deposits across the world. Table 1 highlights countries with the largest concentration ratio of REEs.



Element, Symbol	Concentration Ratio of Rare Earth Element in Some Major Ores of Rare Earth (mass%)						
	Monazite	Bastnaesite		Xenotime	Ion Adsorption-Style Deposit		
	Australia	United States	China	Malaysia	Longnan	Xinfeng	Xunwu
Yttrium, Y	2.4	0.1	–	61.0	62.3	27.5	15.4
Lanthanum, La	23.9	33.2	23.0	1.2	1.8	26.5	31.3
Cerium, Ce	46.0	49.1	50.0	3.1	0.2	2.4	3.4
Praseodymium, Pr	5.0	4.3	6.2	0.5	0.9	6.0	8.7
Neodymium, Nd	17.4	12.0	18.5	1.6	3.8	20.0	28.1
Samarium, Sm	2.5	0.8	0.8	1.1	2.8	4.0	5.3
Europium, Eu	0.1	0.1	0.2	–	–	0.8	0.6
Gadolinium, Gd	1.5	0.1	0.7	3.5	5.7	4.0	4.5
Terbium, Tb	–	–	0.1	0.9	1.2	0.6	0.5
Dysprosium, Dy	0.7	–	0.1	8.3	8.4	4.0	1.2
Holmium, Ho	0.1	–	–	2.0	1.8	0.8	0.1
Erbium, Er	0.2	–	–	6.4	5.1	1.8	0.3
Thulium, Tm	–	–	–	1.1	0.8	0.3	0.1
Ytterbium, Yb	0.1	–	–	6.8	4.6	1.2	0.5
Lutetium, Lu	–	–	–	1.0	0.6	0.1	<0.1

Table 1: Concentration Ratio of Rare Earth Element in Some Major Ores of Rare Earth

There are only a handful of countries that contains concentration of rare earth deposits. Although rare earth is of abundance in nature, it's not easily obtained in high concentration ratio. Therefore, the countries with highest concentrations of monazite, bastnaesite, and xenotime are in position to profit and dominate the industry. In its raw form, an ore of rare earth is not worth much until it is processed. Therefore, once a monazite or bastnaesite is obtained, it goes through a leaching, roasting or chlorination process to yield a rare earth salt such as neodymium chloride. Figure 5 outline the entire process from obtaining the ores of rare earth to yielding the pure rare earth metals.

Phosphate minerals, which are typically monazite, are first dissolved with concentrated sulfuric acid or sodium hydroxide. Solids are then precipitated from the dissolution and those solids are dissolved again with hydrochloric acid. Afterwards, crude rare earth chlorides are extracted through various reductions methods followed by solvent extraction to obtain the individual rare earth elements. For carbonate minerals or, bastnaesites, are dissolved with hydrochloric acid and are separated through solvent extractions [5]. For example, neodymium can be extracted from neodymium chloride using a reduction reaction.

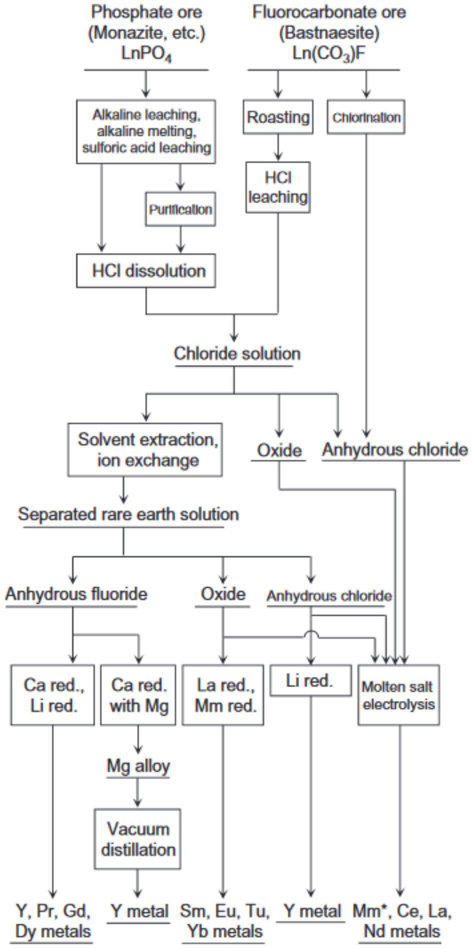


Figure 5: Flow of Rare Earth Metallurgical Processes

The three main reduction methods for producing metallic neodymium are; oxide electrolysis using fluoride salts, electrolysis of chloride salts and calciothermic reduction. An analysis of each method will reveal the advantages and disadvantages of each process while highlighting the environmental impact and cost of production.

3.1 Electrolysis using Fluoride Salt: Electrochemical Reduction Process

The most common production method of neodymium is the electrolysis of neodymium oxide. Neodymium oxide is the main starting material and it is fed to a liquid NdF_3-LiF electrolyte. The neodymium is reduced at the tungsten cathode in the cell center where the liquid neodymium drops in a molybdenum crucible from where it is taken out periodically by a ladle. At the graphite anode, the complex oxide ions are oxidized and oxygen reacts to form gasses of CO and CO_2. At higher voltages and current densities, fluorine ions can oxidize anodically and form perfluorinated carbons (PFC) like CF_4 and C_2F_6 with a tremendous greenhouse gas potential [6]. This process takes place at 1050°C and is able to mass produce commercial grade neodymium.

3.1.1 Electrochemistry of the Fluoride System

Dissolving neodymium oxide and the electrode reactions are dependent on the ionic liquids. The most likely reactions are

1. Dissolution of neodymium oxide:

   $$Nd_2O_3 + [NdF_6]^{3-} + 9F^{-} \rightarrow 3[NdOF_5]^{4-}$$

2. Anodic reaction:

   $$[NdOF_5]^{4-} - 2e^{-} \rightarrow \frac{1}{2} O_2 + Nd^{3+} + 5F^{5-}$$

3. Cathodic reaction:

   $$[NdF_6]^{3-} + 3e^{-} \rightarrow Nd^{0} + 6F^{-}$$

The electrolysis diagram in Figure 6 shows how the neodymium metal is being collected during the anodic reaction and CO_2 is being formed during the cathodic reaction.

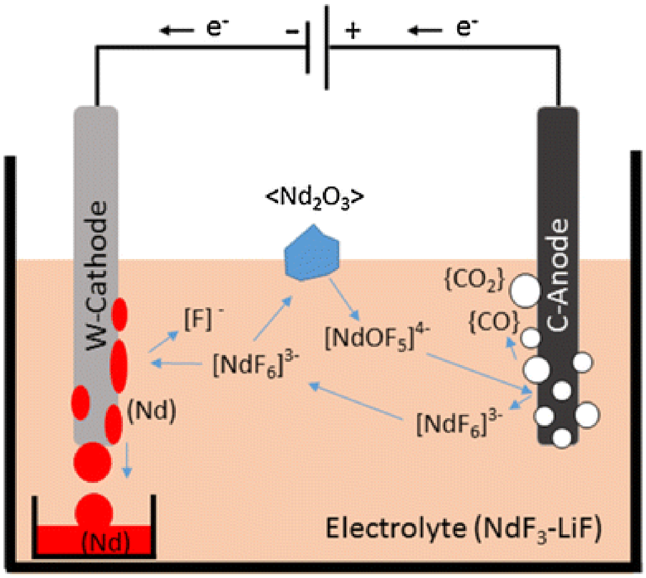
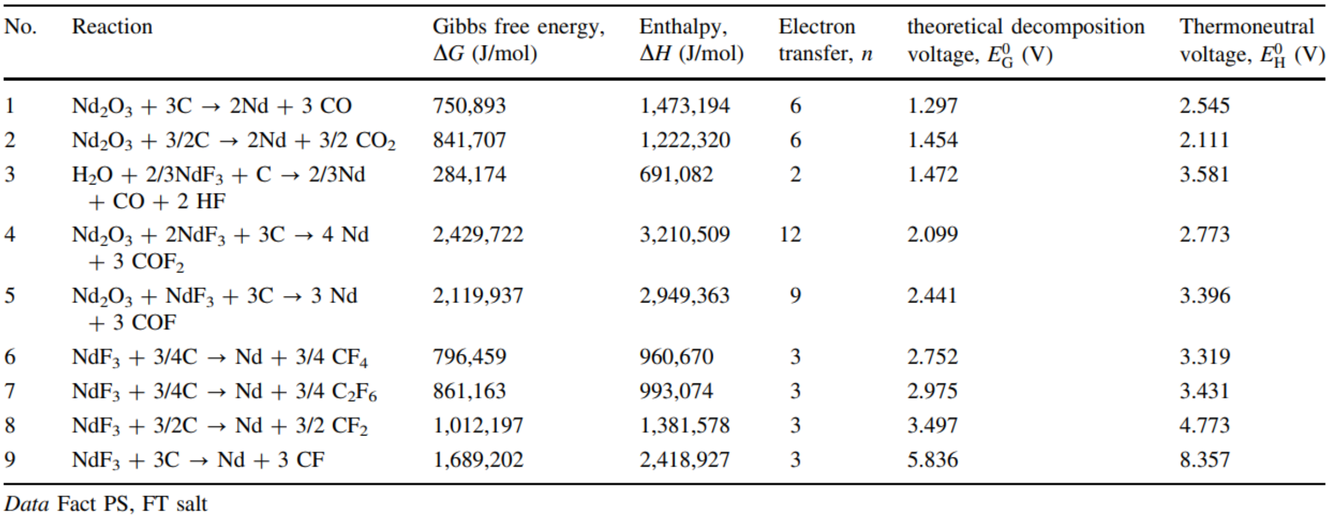


Figure 6: Neodymium Oxide Electrolysis [6]

The neodymium oxide particles dissolve in the electrolyte that consist of approximately 85% neodymium fluoride and 15% lithium fluoride, as seen in Figure 6. The dissolution results in the formation of $[NdOF_5]^{4-}$ while the positively charged electrode of an electrolytic cell evolved O_2 further reacts with carbon to form CO and CO_2. The free Nd^{3+} and F^- ions form the $[NdF_6]^{3-}$ complex ions which then react with the negatively charged electrode of an electrolytic cell to form liquid neodymium and $6F^-$. The positively charged electrode of an electrolytic cell is the negatively charged terminal and the negatively charged electrode of an electrolytic cell is the positively charged terminal.

3.1.2 PFCs and Environmental Impact

Due to the complex ion forms during this process, there are a tremendous amount of other possible reactions that take place based on the reaction mechanism. Table 2 lists the reactions that are likely to happen during the electrolysis. The anodic reactions take place at a very low voltage while thermodynamically the first reaction that happens to form carbon monoxide and carbon dioxide. Once the voltage is slightly increasing, the cooxidation of oxide and fluoride is enable and reacts with carbon to form a very unstable compound in COF_2. COF molecules are also formed in the process which further reacts with carbon to form CF_4, CF_6 and CO.



No.	Reaction	Gibbs free energy, ΔG (J/mol)	Enthalpy, ΔH (J/mol)	Electron transfer, n	theoretical decomposition voltage, E^0_G (V)	Thermoneutral voltage, E^0_H (V)
1	$Nd_2O_3 + 3C \rightarrow 2Nd + 3\,CO$	750,893	1,473,194	6	1.297	2.545
2	$Nd_2O_3 + 3/2C \rightarrow 2Nd + 3/2\,CO_2$	841,707	1,222,320	6	1.454	2.111
3	$H_2O + 2/3NdF_3 + C \rightarrow 2/3Nd + CO + 2\,HF$	284,174	691,082	2	1.472	3.581
4	$Nd_2O_3 + 2NdF_3 + 3C \rightarrow 4\,Nd + 3\,COF_2$	2,429,722	3,210,509	12	2.099	2.773
5	$Nd_2O_3 + NdF_3 + 3C \rightarrow 3\,Nd + 3\,COF$	2,119,937	2,949,363	9	2.441	3.396
6	$NdF_3 + 3/4C \rightarrow Nd + 3/4\,CF_4$	796,459	960,670	3	2.752	3.319
7	$NdF_3 + 3/4C \rightarrow Nd + 3/4\,C_2F_6$	861,163	993,074	3	2.975	3.431
8	$NdF_3 + 3/2C \rightarrow Nd + 3/2\,CF_2$	1,012,197	1,381,578	3	3.497	4.773
9	$NdF_3 + 3C \rightarrow Nd + 3\,CF$	1,689,202	2,418,927	3	5.836	8.357

Data Fact PS, FT salt

Table 2: Theorical decomposition enthalpies and corresponded voltages of neodymium oxide reactions at 1050 °C using FactSage

The products at higher voltages are referred to as perfluorinated carbons (PFC) and the emission of these gases are harmful to the environment. They are some of the most potent greenhouse gases, with global warming potential 6000-10,000 times higher than CO_2. It's very unlikely that the systems being used to filter and treat greenhouse gases are not capturing the PFCs that the process is emitting. As governments are looking for ways to cut down on greenhouse gas emissions, this process would less likely be implemented here in the U.S., unless PFC emission can be avoided. The cost of operating the process at 1050 °C is disadvantageous to any business bottom line.

3.2 Electrolysis using Chloride Salts

The electrodeposition of rare earth using chloride salts has proven to be less costly than using fluoride salts. Using chloride salts eliminates the greenhouse gas emissions that is present in the electrolysis using fluoride salts. This method is currently being used in China to produce mischmetal; which is a mixed of rare earth metals such ad La, Ce, Pr, and Nd. The starting materials for producing the mischmetal are crude rare earth chlorides hexahydrate.

3.2.1 Electrochemistry of the Chloride System

The first part of the process is removing the water from the rare earth hexahydrate through drying. The dehydration is important in this process because the water in the raw material will significantly decrease current efficiency in the electrolytic bath and erode the graphite anode. The dehydration is carried out at 400-450°C; to avoid the formation of the rare earth oxychloride and HCl which occurs when the temperature is too high. The rare earth oxychlorides do not dissolve in the electrolytic bath and accumulates at the bottom of the cell which decreases the yield and contaminates the final product metal. It’s critical to control the drying temperature in this process and keep the anhydrous rare earth chlorides under dry atmosphere to avoid absorbing moisture.

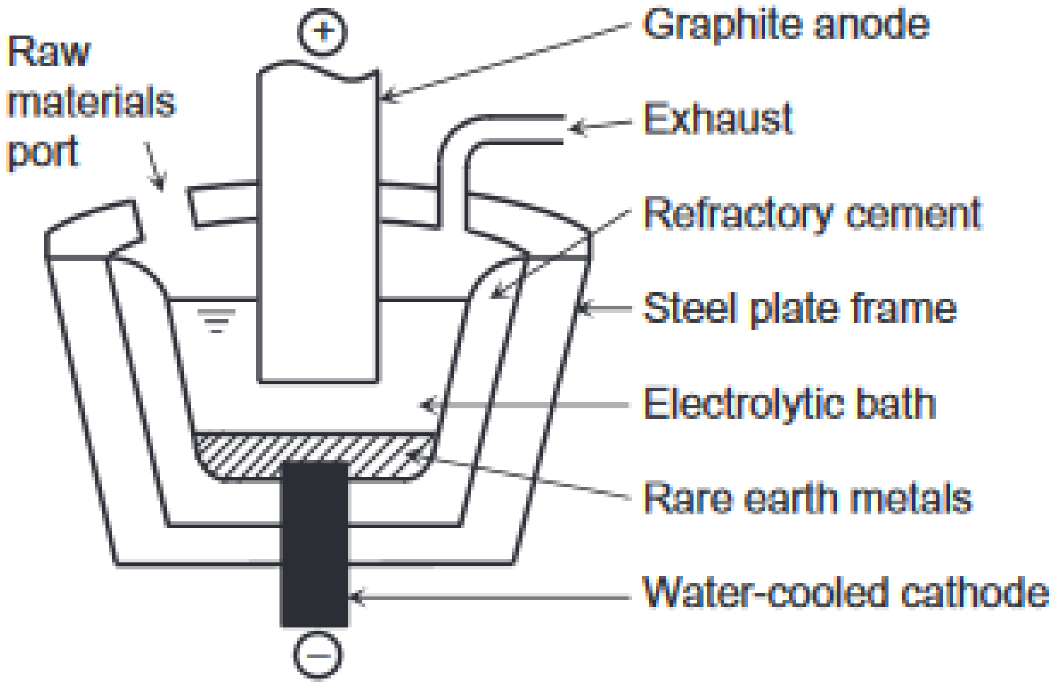


Figure 7: Electrolytic Cell for Molten Chloride Electrolysis

The electrolytic cell in Figure 7 in which the electrodes are facing each other at the top and bottom is usually used for this process. The cathode is made up of steel, synthetic graphite, molybdenum, and tantalum while the anode is just synthetic graphite.

In the case of producing the neodymium metal, neodymium chloride hexahydrate is dried to completion to obtain neodymium chloride. The neodymium chloride mixed with 5-10% of NaCl and KCl are charged into the electrolytic cell via the raw materials port. The electrolysis is then carried out at a temperature range of 850-950 °C and at a voltage range of 5-12V. The electrochemical reactions as follow

1. Cathodic Reaction:
    a. $Nd^{3+} + 3e^- \rightarrow Nd(l)$
2. Anodic Reaction:
    a. $2Cl^- \rightarrow Cl_2(g) + 2e^-$
3. Overall Reaction:
    a. $NdCl_3 \rightarrow Nd(l) + 3/2Cl_2(g)$

The liquid neodymium metals forms and accumulates on the cathode, and it works as liquid cathode. At the anode, chlorine gas is generated and the salt level in the bath decreases as the electrolysis progresses. This can be a semi-continuous process as more neodymium chloride can be added every time the salt level decreases.

3.3 Calciothermic Reduction Process

This project focuses on the third method- calciothermic reduction with magnesium to produce neodymium-magnesium master alloy. The calciothermic reduction process was also modeled using zinc instead of magnesium to produce a neodymium-zinc alloy, however, that process cannot take place in an iron crucible. Using zinc would be costlier but would produce 89 weight percent of neodymium in the master alloy. The thermodynamic modeling was the main focus for the WPI team while the Terves team was responsible for carrying out the experiments and has the potential to scale up this process. Ames Laboratory has been doing the purification to pure Nd and characterization of the master alloy obtained from Terves' experiments.

Calciothermic reduction is a novel technique being studied across the industry. The idea is for a displacement reaction to happen under certain conditions where the calcium displaces the rare earth element in the rare earth salt as follow:

$$2RECl_3 + 3Ca \rightarrow 2RE + 3CaCl_2$$

The reduction process also includes some other forms of metal such as Magnesium to form a master alloy with the rare earth metal. The magnesium is removed through vacuum distillation from the master alloy, therefore, choosing a metal that can be easily distilled is crucial for the calciothermic reduction. Molten salts such as sodium chloride and potassium chloride are used as solvent in the calciothermic reduction process.

4 Methodology

Using FactSage as the only computing software, the ternary phase diagram was generated for multiple neodymium systems. The systems that will be discussed in this report are Nd-Ca-Cl, Nd-Mg-Cl, Nd-Zn-Ca, and Nd-Fe-Zn. Following the phase diagram, the equilibrium quantities and phase compositions are computed as a function of initial amounts.

4.1 Phase one

The ternary diagram in FactSage ensure the different phases that exist between any three-component system. The ternary diagram was computed for the following systems:

1. Nd-Ca-Cl
2. Nd-Mg-Cl
3. Nd-Zn-Ca
4. Nd-Fe-Zn
5. Nd-Mg-Cr
6. Nd-Mg-Fe
7. $NdCl_3$-NaCl-KCl

These diagrams will be used along with the equilibrium calculations to form the thermodynamic models to be provided to Terves. The calculations complete showing the yield as well as purity at different temperature for optimize results of calcium and magnesium reaction with neodymium chloride in molten salt. Thermodynamic model for producing Nd-Mg master alloy with magnesium as the reducing agent as well as producing neodymium with calcium as the reducing agent.

4.2 Phase two

Calculations are complete which help visualize and understand the 7-component Nd-Ca-Mg-Zn-K-Na-Cl system, including equilibrium between the chloride phase and one or more metal phases including intermetallic compounds. Calculation complete for Calciothermic Reduction, Calciothermic Reduction in Magnesium, and Calciothermic Reduction in Zinc

A thermodynamics model is also complete for reducing $NdCl_3$ in mixed salt with NaCl and KCl, including three composition-temperature designs for producing Mg-Nd master alloy with Mg as reducing agent, three designs for producing Nd-Zn master alloy with Ca as the reducing agent, and two designs for producing Nd with Ca as the reducing agent.

I also, analyzed the reduction process of neodymium oxychloride. However, FactSage does not contain a database which includes the rare earth oxychloride. An analytical approach was taken in an attempt to understand the neodymium oxychloride reduction process. Other options such as using ThermoCalc software are being explored for modeling the process using neodymium oxychloride.

5 Results and Discussions

This section will explain the results of the calciothermic reduction process and using Magnesium and Zinc as additional metals to improve neodymium output. An analytical approach was attempted to study the process using neodymium oxychloride briefly highlights Terves completed experiments.

Given the focus, thermodynamic modeling for the process was studied using FactSage. A combination of ternary phase diagrams and equilibrium calculations were utilized to determine the ideal and cost-effective method of producing commercial grade purity of neodymium through the calciothermic reduction process. Given that the process is highly inefficient by just using calcium and molten salts as solvents, such as sodium chloride and potassium chloride, the process was studied using the presence of other metals such as magnesium and zinc to improve efficiency and output of neodymium. For cost purposes, all of the reactions are taking place in an iron crucible at a temperature range of 600°C to 800°C and 1 atmospheric pressure.

Using ternary thermodynamic models of the Nd-Ca-Cl and Nd-Mg-Cl systems to describe the metallothermic reduction of $NdCl_3$ by using Ca or Mg. Candidate operating temperatures are 700°C, 800°C, and 900°C. Results show reduction by Ca will likely succeed, though reduction by Mg will not work as planned. Used FactSage to build thermodynamic models of the Nd-Ca-Mg-K-Na-Cl-Fe and Nd-Ca-Zn-K-Na-Cl-Fe systems, and literature phase diagrams, to inform process design for metallothermic reduction of $NdCl_3$ using Ca with Mg or Zn solvent.

5.1 Calciothermic Reduction

Calcium reduction of neodymium chloride follows the reaction:

$$2\ NdCl_3 + 3\ Ca \rightarrow 2\ Nd + 3\ CaCl_2$$

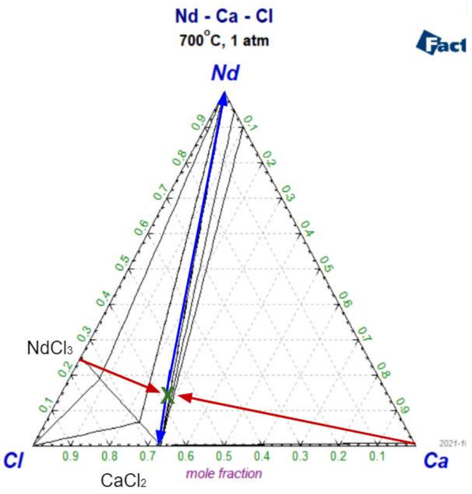


Figure 8: Calculated Nd-Ca-Cl Phase Diagram at 700°C using FactSage

The Nd-Cl-Ca phase diagram in Figure 8 represents this with 8 moles of atoms in $NdCl_3$ (two Nd, six Cl) and three moles of Ca atoms (tails of red arrows) reacting to form 2 moles of Nd and 9 of $CaCl_2$ atoms (three Ca, six Cl) (heads of blue arrows). The green X shows the average composition: 27% Nd 54% Cl 18% Ca. The diagrams show that equilibrium is possible between $CaCl_2$ salt with very low $NdCl_3$ concentration, and Nd metal with very low Ca concentration.

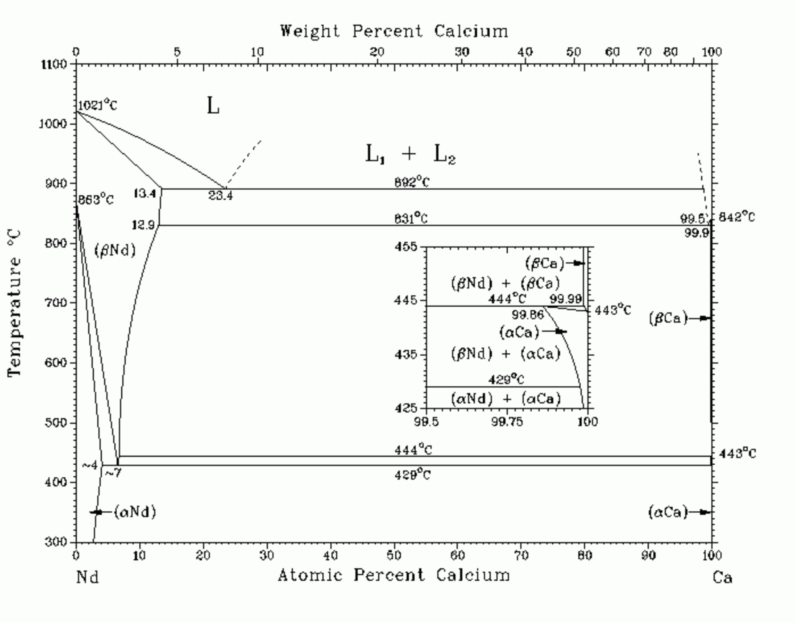


Figure 9: Ca-Nd Metal Phase Diagram

700°C is below the melting points of the chlorides, yet above their eutectic. Therefore, leading to a liquid region between the chlorides. 800°C is above both chlorides melting points, causing the whole thing to be liquid. In Figure 9, the Ca-Nd metal phase diagram shows the metals are mostly immiscible. There is a high-T BCC β-Nd phase which is stable from 863° to the melting point where calcium stabilizes. This is shown in the ternary diagrams as a solid solution.

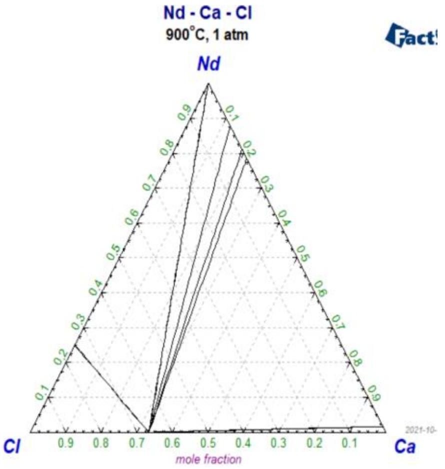


Figure 10: Calculated Nd-Ca-Cl Phase Diagram at 900°C Using FactSage

In principle, it's possible to combine reactants at stoichiometric ratios to make the products. The 700°C diagram shows that the reactants are solid. At 800°C chlorides are liquid but Ca and Nd metals are solids, potentially limiting the reaction. At 900°C Ca and chlorides are liquids. This is likely the best temperature for calciothermic reduction.

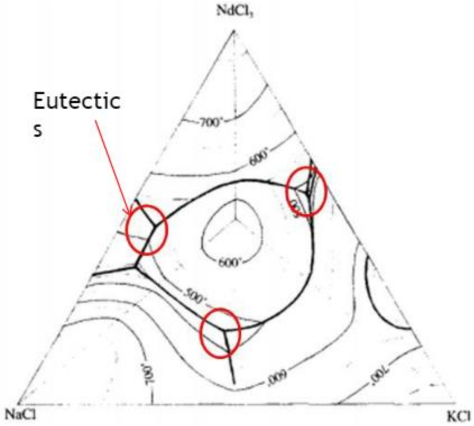


Figure 11: $NdCl_3$-NaCl-KCl Liquidous Projection

Figure 11 shows the liquidus projection for $NdCl_3$-NaCl-KCl which illustrates ternary eutectic compositions that melts under 500°C. The molten salt of NaCl-KCl is a good solvent for dissolving $NdCl_3$ due to the low eutectic. Throughout the equilibrium calculation and the experiments, the NaCl-KCl molten salt was used as the preferred solvent.

Using 166.75g $NdCl_3$ + 40g Ca gives approximate stoichiometry. $NdCl_3$ can be diluted by 396.5g NaCl + 460.6g KCl to form a liquid at 700°C. At 700°C, these reactants equilibrate to:

- 940.9 g liquid salt: 37.27 wt% NaCl 48.96% KCl 11.77% $CaCl_2$ 0.03% $NdCl_3$
- 95.97 g Nd metal with just ppb levels of Ca

Yield and product purity are high; there's little $NdCl_3$ remaining in the salt and almost no Ca in the product. Though 900°C is likely the best temperature for calciothermic reduction, practical considerations make lower temperatures better. Nonetheless, the team looked into dilution with Zn and Mg.

5.2 Calciothermic Reduction in Magnesium

Magnesium reduction of neodymium chloride would follow the same reaction but does not run to completion due to the different reaction-free energy. That is unlike the Ca-Nd system, where Ca reduces $NdCl_3$, in the Mg-Nd system, Nd reduces $MgCl_2$.

Figure 12: Nd-Mg-Cl phase diagrams at 660°C (left) and 800°C (right) showing Mg-Nd alloy with low Nd concentration in equilibrium with $MgCl_2$-$NdCl_3$ salt having high Nd concentration.

The WPI team hypothesis was that Mg could react with $NdCl_3$ to produce a Mg-Nd master alloy at a high yield with low $NdCl_3$ in the salt. Unfortunately, the phase diagrams in Figure 11 show that regardless of temperature metal compositions with low Mg concentration are in equilibrium with chlorides with high $NdCl_3$ concentration. At higher temperatures this is more the case. At 800°C nearly pure $NdCl_3$ is in equilibrium with many solid and solid-liquid compositions. But even at 660°C salts with high $MgCl_2$ and low $NdCl_3$ are only in equilibrium with Mg alloys with very little Nd. Mg-Nd master alloy production will likely not be possible via this route.

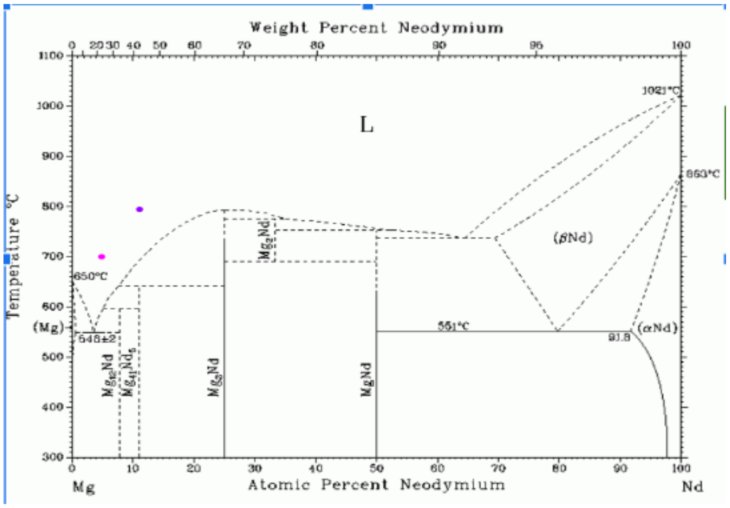


Figure 13: Nd-Mg Metal Phase Diagram

The Mg-Ca and Mg-Nd phase diagrams in Figure 13show low eutectics, and both share low iron solubility, making a mild steel crucible an option. Chromium also have low solubility in both magnesium and calcium which makes it an option to use 400 series stainless steels for the crucible. The main design uses (458.1g Mg + 40g Ca) liquid + (166.75 g $NdCl_3$ + 396.5 g NaCl + 460.6 g KCl) liquid at 700° or 800°C to form:

- 945.55g liquid salt: 39.05% NaCl 11.71% $CaCl_2$ 48.71% KCl 0.526% $MgCl_2$ 0.03% $NdCl_3$
- 557.70g liquid metal: 81.91 wt.% Mg 18.07% Nd 0.0164% Na

One can also reduce the amount of Mg at 800°C to 160g, which forms:

- 945.58g liquid salt: 39.07 wt% NaCl 11.71% $CaCl_2$ 48.71% KCl 0.51% $MgCl_2$
- 259.6g liquid metal: 259.57 g liquid metal 61.17 wt.% Mg 38.82% Nd 0.01% Na

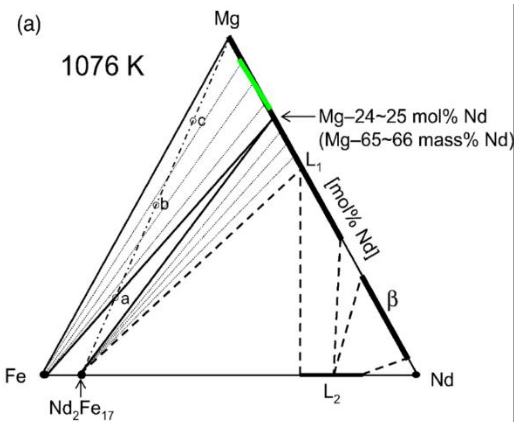


Figure 14: Mg-Nd-Fe ternary phase diagram showing low iron solubility in liquid up to 66 wt% Nd.

This last design is better because it uses less Mg and requires less distillation to produce Nd. However, it requires processing at 800°C, which is less advantageous than 700°C. All three designs have product compositions compatible with an iron crucible as shown in Figure 14.

Note that the absence of full FactSage data on $NdCl_3$ activity in the $NdCl_3$-NaCl-KCl system prevents this model from predicting Nd reduction yield. The model treats $NdCl_3$ as having unit activity, leading to prediction of 100% yield. In reality, the activity declines with mole fraction, and Mg-Nd master alloy with high Nd, such as that in the last design, will correspond with higher equilibrium $NdCl_3$ concentration in the salt phase, and lower Nd reduction yield. It would be helpful to be able to predict this effect on yield, as well as kinetics limitations, so Terves can use this tool to choose the best design trading off between low Mg which reduces distillation cost, vs. high Mg which likely improves Nd reduction yield.

5.3 Calciothermic Reduction in Zinc

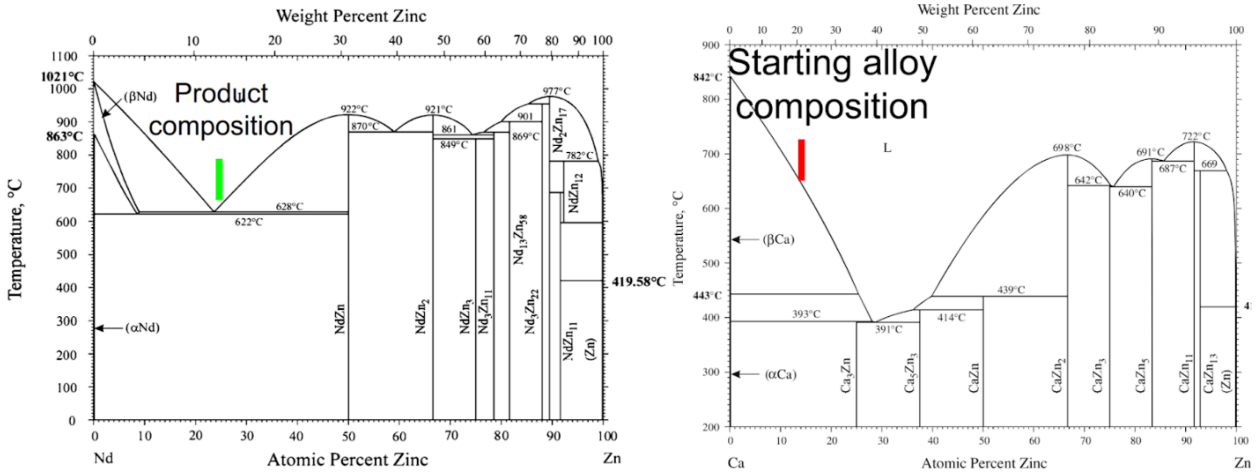


Figure 15: : Ca reduction with Zn dilution showing product composition and temperature range

The Zn-Ca and Zn-Nd phase diagrams in *Figure 15* shows eutectic liquids above 650°C when combined in mole ratios 4:1 and 5:1 respectively. This leads to the designs: (40g Ca + 12g Zn) liquid + (166.75g $NdCl_3$ + 369.5g NaCl + 460.6g KCl) liquid at 650°, 700° or 725°C which forms:

- 940.9g liquid salt: 39.3 wt% NaCl 49.7% KCl 11.7% $CaCl_2$ 0.03% $NdCl_3$
- 108.0g liquid metal: 88.9 wt% Nd 11.1% Zn

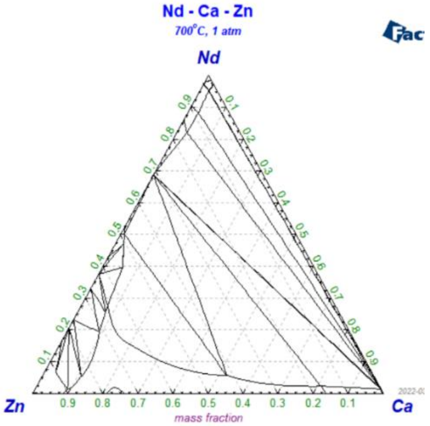


Figure 16: Zn-Ca-Nd Ternary Phase Diagram using FactSage

This system has the advantages of liquid reactants and products. Though, it must “cross” an intermetallic region in the phase diagram which could form solids and slow the reaction. One issue is that this liquid metal product has significant iron solubility. The iron solubility will prevent the use of an iron crucible. Coatings such as yttria or BN could work. However, oxides such as alumina may react with the Nd in this product alloy.

5.4 Analytical Approach for NdOCl

Since FactSage could not be used to calculate ternary phase and equilibrium for NdOCl as it does not contain the NdOCl database, an analytical modeling was developed to compare the stability field diagram for NdOCl with CaCl/CaO and MgCl/MgO.

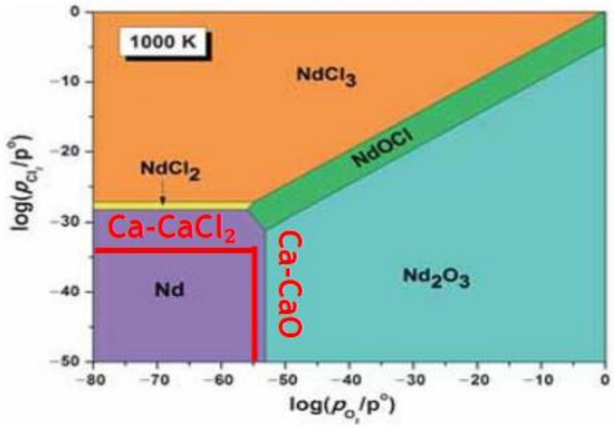


Figure 17: Stability Field Diagram for the Nd-O-Cl System at 1000K

The red line on the vertical axis in the stability field diagram in *Figure 17* shows the partial pressure of Oxygen for CaO while the horizontal line shows the partial pressure of Chlorine for $CaCl_2$. The equilibrium equation for calcium oxide (1) and calcium chloride (2) is

1. $2Ca + O_2 \rightarrow 2CaO$
2. $Ca + Cl_2 \rightarrow CaCl_2$

And using the Gibbs free energy equation

$$\Delta G = \Delta H - T\Delta S$$

Along with thermodynamic data from NIST chemistry webbook, the partial pressure of oxygen was determined as follow:

$$\Delta_f H^\circ(298.15K) = -1269.84 \text{ kJ/mol}$$
$$\Delta G(1000K=727^\circ C) = -1044.90 \text{ kJ/mol}$$
$$\Delta G = \Delta G^\circ + RT\ln(pO_2/1atm) = 0$$
$$pO_2 = 1atm\cdot\exp(\Delta G^\circ/RT) = 10^{-55} \text{ atm}$$

and the partial pressure for chlorine determined as:

$$\Delta H^\circ(298.15K) = -795.80 \text{ kJ/mol}$$
$$\Delta G(1000K=727^\circ C) = -652.30 \text{ kJ/mol}$$
$$pCl_2 = 1atm\cdot\exp(\Delta G/RT) = 10^{-34} \text{ atm}$$

Which lead to the conclusion that calcium tends to be more stable to lower oxygen and chlorine content than neodymium.

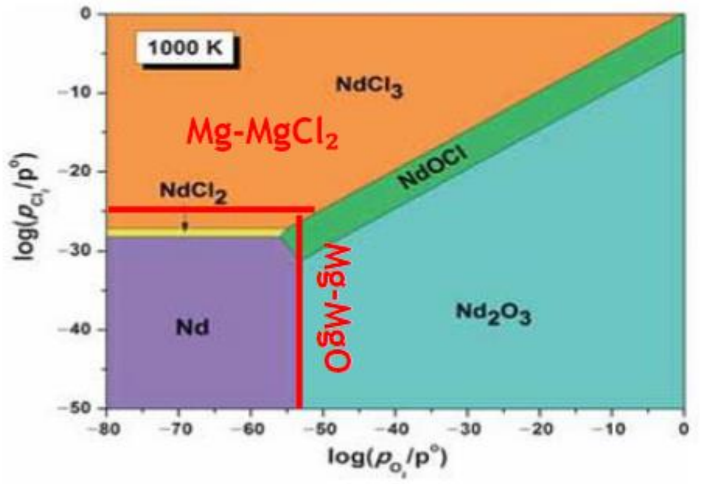


Figure 18: Stability Field Diagram for the Nd-O-Cl System at 1000 K

Similarly, using the stability field diagram in *Figure 18* and Gibbs free energy, the partial pressure of oxygen for MgO and the partial pressure of chlorine for $MgCl_2$ was determined. For Magnesium Oxide the equilibrium equation is

$$2Mg + O_2 \rightarrow 2MgO$$

And the Gibbs free energy calculation to obtain the partial pressure of oxygen is

$$\Delta_f H°(298.15K)=-1203.2\ kJ/mol$$
$$\Delta G(1000K=727°C)=-1104.7\ kJ/mol$$
$$\Delta G=\Delta G°+RT\ln(pO_2/1atm) = 0$$
$$pO_2 = 1atm\cdot\exp(\Delta G°/RT) = 10^{-58}\ atm$$

The equilibrium equation for magnesium chloride is

$$Mg + Cl_2 \rightarrow MgCl_2$$

And the Gibbs free energy calculation to obtain the partial pressure of chlorine is

$$\Delta H°(298.15K)=-641.62\ kJ/mol$$
$$\Delta G(1000K=727°C)=-472.44\ kJ/mol$$
$$pCl_2 = 1atm\cdot\exp(\Delta G/RT) = 10^{-25}\ atm$$

Therefore, magnesium tends to have less affinity for chlorine than neodymium.

Thus, stripping chlorine from $NdCl_3$ with magnesium and calcium is not that different than stripping oxygen and chlorine from NdOCl.

5.5 Terves Experimental Results

The Terves team carried out several reduction experiments. A total of 11 runs completed at various conditions and under different orders of operation from NdOCl and $NdCl_3$. All reactions were done under inert gas at a temperature range of 700°C to 800°C with batch sizes of 500 mL to one liter. 15 minutes of mixing is required after all the reactants are molten at the processing time and the reaction is allowed to settle from zero to two hours.

Terves has confirmed that Ca reduction of NdOCl can produce Nd-Mg alloy at 750°C. To obtain the neodymium metal to be used for Nd-Fe-B magnets, the Nd-Mg alloy will be distilled. The distillation of the master alloy was carried out by Ames laboratory where a 60 wt% Nd metal was obtained.

6 Conclusions and Recommendations

The thermodynamic modeling of the calciothermic reduction process confirmed that calcium is a good reductant for reducing neodymium chloride. Potassium chloride and sodium chloride eutectic proves to be a good solvent for neodymium chloride. Magnesium and zinc are solvents for neodymium to form the desired master alloy. Both magnesium and zinc have high vapor pressure and can be distilled from the master alloy. However, magnesium-neodymium master alloy is more compatible with an iron crucible than the zinc-neodymium master alloy.

Although an analytical approach was taken to analyze the neodymium oxychloride, the results obtained are not as detailed as that of neodymium chloride. Therefore, further investigation is needed on neodymium oxychloride thermodynamics and reaction temperature to achieve optimal results. Further analysis is required to scale the neodymium chloride production as well as calciothermic reduction process. All experiments and models have been completed for lab scale composition. The next phase will be obtaining the max composition that can run at the temperature range of 700°C to 800°C. Batch sizes will also increase as well as the mixing time and settling time. The distillation process would require scaling up since Ames Laboratory has only been working on distilling small batches of neodymium-magnesium master allow.

A low-cost metal distillation technology can be incorporated to further reduce the cost of production in scaling up this process. This technology can reduce the energy requirement of the overall production process and is referred to as Gravity Multiple Effect Thermal System, or GMETS

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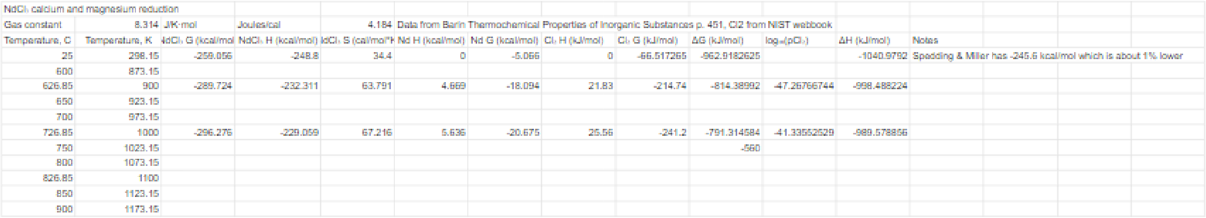
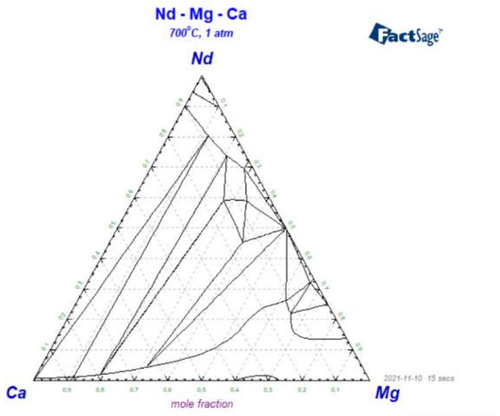
Appendix

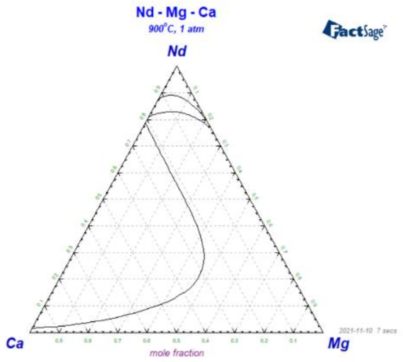
Analytical Calculation



NdCl$_3$ calcium and magnesium reduction												
Gas constant	8.314	J/K·mol	Joules/cal	4.184	Data from Barin Thermochemical Properties of Inorganic Substances p. 451, Cl2 from NIST webbook							
Temperature, C	Temperature, K	ldCl$_3$ G (kcal/mol	NdCl$_3$ H (kcal/mol)	ldCl$_3$ S (cal/mol°	Nd H (kcal/mol)	Nd G (kcal/mol)	Cl$_2$ H (kJ/mol)	Cl$_2$ G (kJ/mol)	ΔG (kJ/mol)	log$_{10}$(pCl$_2$)	ΔH (kJ/mol)	Notes
25	298.15	-259.056	-248.8	34.4	0	-5.066	0	-66.517265	-962.9182625		-1040.9792	Spedding & Miller has -245.6 kcal/mol which is about 1% lower
600	873.15											
626.85	900	-289.724	-232.311	63.791	4.669	-18.094	21.83	-214.74	-814.38992	-47.26766744	-998.488224	
650	923.15											
700	973.15											
726.85	1000	-296.276	-229.059	67.216	5.636	-20.675	25.56	-241.2	-791.314584	-41.33552529	-989.578856	
750	1023.15								-560			
800	1073.15											
826.85	1100											
850	1123.15											
900	1173.15											

Sample FactSage Ternary Diagrams





Sample FactSage Equilibrium Calculation

FactSage 8.0

(gram) 175.05 NdCl3 + 12 Zn + 40 Ca + 369.5 NaCl +

(750,1,s-FactPS,#1) (750,1,s6-FTlite,#1) (750,1,s1-FThall,#1) (750,1,s-FTfrt

(gram) 460.6 KCl =

(750,1,s-FTfrtz,#1)

940.87 gram Salt-liquid#1

(940.87 gram, 13.499 mol)

\+ 0 gram Salt-liquid#2

(750 C, 1 atm, a=1.0000)

(39.272 wt.% NaCl

```
          + 48.955     wt.% KCl

          + 11.773     wt.% CaCl2

          + 6.1604E-12 wt.% ZnCl2)


          Site fraction of sublattice constituents:

          Na[+]                  0.46837

          K[+]                   0.45769

          Ca[2+]                 7.3937E-02

          Zn[2+]                 3.1506E-14

          -----------------------------------

          Cl[-]                  1.0000


          System component         Amount/mol    Amount/gram   Mole fraction  Mass fraction

          Zn                     4.2529E-13     2.7805E-11     1.5191E-14     2.9553E-14

          Ca                     0.99805        40.000         3.5650E-02     4.2514E-02

          K                      6.1783         241.56         0.22069        0.25674

          Cl                     14.497         513.96         0.51783        0.54626

          Na                     6.3224         145.35         0.22584        0.15449


      + 107.97     gram  Liquid#1

       (107.97 gram, 0.84891 mol)

      + 0          gram  Liquid#2

          (750 C, 1 atm,     a=1.0000)

          ( 5.7612E-08 wt.% Ca

          + 2.6398E-08 wt.% K

          + 4.0111E-07 wt.% Na

          + 88.886     wt.% Nd
```

```
        + 11.114     wt.% Zn)

        System component         Amount/mol    Amount/gram   Mole fraction  Mass fraction
        Nd                     0.66537        95.974         0.78379        0.88886
        Zn                     0.18354        12.000         0.21621        0.11114
        Ca                     1.5521E-09     6.2206E-08     1.8284E-09     5.7612E-10
        K                     7.2900E-10     2.8503E-08     8.5875E-10     2.6398E-10
        Na                     1.8839E-08     4.3309E-07     2.2191E-08     4.0111E-09

+ 0         gram  BCC-A2#1
+ 0         gram  BCC-A2#2
        (750 C, 1 atm,     a=0.93606)
        ( 3.7010E-08 wt.% Ca
        + 2.5794E-09 wt.% K
        + 5.4868E-08 wt.% Na
        + 96.582     wt.% Nd
        + 3.4175     wt.% Zn)

+ 0         gram  Salt-liquid2#1
+ 0         gram  Salt-liquid2#2
        (750 C, 1 atm,     a=0.91395)
        ( 47.245     wt.% NaCl
        + 52.755     wt.% KCl)

+ 0         gram  Liquid3
        (750 C, 1 atm,     a=0.91342)
        ( 52.714     wt.% KCl
```

```
     + 47.286     wt.% NaCl)

+ 0       gram  DHCP-A3'
     (750 C, 1 atm,     a=0.87349)
     ( 100.00     wt.% Nd
     + 3.2978E-09 wt.% Ca)

+ 0       gram  FCC-A1#1
+ 0       gram  FCC-A1#2
     (750 C, 1 atm,     a=0.82430)
     ( 1.5150E-08 wt.% Ca
     + 3.3964E-09 wt.% K
     + 3.6147E-08 wt.% Na
     + 3.7161E-02 wt.% Zn
     + 99.963     wt.% Nd)

+ 0       gram  Rocksalt#1
+ 0       gram  Rocksalt#2
+ 0       gram  Rocksalt#3
     (750 C, 1 atm,     a=0.72034)
     ( 53.699     wt.% NaCl_halite
     + 46.090     wt.% KCl_sylvite
     + 0.14358    wt.% CaCl[+]
     + 2.3768E-14 wt.% ZnCl[+]
     + 6.7395E-02 wt.% VaCl[-])

+ 0       gram  Fm3m#1
```

```
+ 0        gram  Fm3m#2
+ 0        gram  Fm3m#3
          (750 C, 1 atm,     a=0.71865)
          ( 52.660     wt.% NaCl
          + 47.340     wt.% KCl)

+ 0        gram  AlkCl-ss#1
+ 0        gram  AlkCl-ss#2
+ 0        gram  AlkCl-ss#3
          (750 C, 1 atm,     a=0.71792)
          ( 52.707     wt.% NaCl
          + 47.293     wt.% KCl)

+ 0        gram  HCP-A3#1
+ 0        gram  HCP-A3#2
          (750 C, 1 atm,     a=0.61455)
          ( 4.7884E-09 wt.% Ca2Va
          + 4.1882E-09 wt.% K2Va
          + 4.7692E-08 wt.% Na2Va
          + 4.9850E-02 wt.% Zn2Va
          + 99.950     wt.% Nd2Va)

+ 0        gram  cubic-Perovskite#1
+ 0        gram  cubic-Perovskite#2
          (750 C, 1 atm,     a=7.3042E-02)
          ( 4.9718E-06 wt.% NaCaCl3
          + 100.00     wt.% KCaCl3_ht)
```

```
+ 0         gram  cubic-Perovskite#3
          (750 C, 1 atm,     a=5.0720E-04)
          ( 99.873     wt.% NaCaCl3
          + 0.12720    wt.% KCaCl3_ht)

+ 0         gram  ortho-Perovskite#1
+ 0         gram  ortho-Perovskite#2
          (750 C, 1 atm,     a=5.0602E-02)
          ( 7.1767E-06 wt.% NaCaCl3
          +100.000     wt.% KCaCl3_lt)

+ 0         gram  ortho-Perovskite#3
          (750 C, 1 atm,     a=5.0702E-04)
          ( 99.913     wt.% NaCaCl3
          + 8.7408E-02 wt.% KCaCl3_lt)

+ 0         gram  C42#1
+ 0         gram  C42#2
          (750 C, 1 atm,     a=4.3826E-02)
          ( 100.00     wt.% NdZn2
          + 1.3222E-08 wt.% CaZn2)

+ 0         gram  Rutile#1
+ 0         gram  Rutile#2
+ 0         gram  Rutile#3
          (750 C, 1 atm,     a=1.1037E-02)
```

```
          ( 100.00     wt.% CaCl2_beta
          + 2.6078E-15 wt.% ZnCl2)

+ 0         gram  Zn-liq
          (750 C, 1 atm,     a=1.2573E-03)
          ( 98.643     wt.% Zn
          + 1.3568     wt.% Na)

+ 0         gram  HCP-Zn#1
+ 0         gram  HCP-Zn#2
          (750 C, 1 atm,     a=9.3239E-04)
          ( 5.8172E-04 wt.% Ca
          + 7.2559     wt.% Na
          + 92.744     wt.% Zn)

+ 0         gram  Liquid2
          (750 C, 1 atm,     a=8.0806E-04)
          ( 1.0825E-04 wt.% Ca
          +100.000     wt.% Na)

+ 0         gram  Liquid-Alloy#1
+ 0         gram  Liquid-Alloy#2
          (750 C, 1 atm,     a=8.0806E-04)
          ( 1.0825E-04 wt.% Ca
          +100.000     wt.% Na)

+ 0         gram  Na-K(BCC)#1
```

```
+ 0         gram  Na-K(BCC)#2
      (750 C, 1 atm,     a=4.7708E-04)
      ( 97.896     wt.% Na
      + 2.1043     wt.% K)

+ 0         gram  BCC#1
+ 0         gram  BCC#2
      (750 C, 1 atm,     a=4.7132E-04)
      ( 5.8724E-04 wt.% Ca
      + 99.999     wt.% Na)

+ 0         gram  FCC
      (750 C, 1 atm,     a=4.0548E-04)
      ( 1.7079E-05 wt.% Ca
      +100.000     wt.% Na)

+ 0         gram  D03#1
+ 0         gram  D03#2
      (750 C, 1 atm,     a=9.9492E-05)
      ( 99.909     wt.% Zn3Nd
      + 8.5208E-02 wt.% Na3Nd
      + 5.8901E-03 wt.% K3Nd)

+ 0         gram  D2d#1
+ 0         gram  D2d#2
      (750 C, 1 atm,     a=1.0276E-08)
      ( 100.00     wt.% NdZn5
```

```
        + 2.1581E-09 wt.% CaZn5)

+ 0         gram  D81
        (750 C, 1 atm,     a=4.9539E-12)
        (100.000     wt.% Nd5Zn3
        + 1.6664E-05 wt.% Ca5Zn3)

+ 0         gram  beta-K2SO4#1
        (750 C, 1 atm,     a=6.2411E-15)
        ( 5.4386E-02 wt.% Na2ZnCl4
        + 99.946     wt.% K2ZnCl4-ht)

+ 0         gram  beta-K2SO4#2
        (750 C, 1 atm,     a=3.0284E-16)
        ( 98.293     wt.% Na2ZnCl4
        + 1.7070     wt.% K2ZnCl4-ht)

+ 0         gram  tI48
        (750 C, 1 atm,     a=3.2376E-24)
        ( 100.00     wt.% NdZn11
        + 1.4658E-10 wt.% CaZn11)

+ 0         gram  hP38
        (750 C, 1 atm,     a=3.7193E-33)
        ( 8.1382E-19 wt.% Ca2Zn17
        + 100.00     wt.% Nd2Zn17)
```

```
+ 0        gram  D23#1

+ 0        gram  D23#2

       (750 C, 1 atm,     a=7.3945E-42)

       ( 4.7661     wt.% NaZnZn4Zn4Zn4

       + 95.234     wt.% CaZnZn4Zn4Zn4)


+ 8.3078     gram  NdCl3_solid

  (8.3078 gram, 3.3152E-02 mol)

       (750 C, 1 atm, S1, a=1.0000)


+ 0        gram  NdCl3_liquid

       (750 C, 1 atm, L1, a=0.95065)


+ 0        gram  Nd_dhcp

       (750 C, 1 atm, S1, a=0.87340)


+ 0        gram  Nd_bcc_A2

       (750 C, 1 atm, S2, a=0.84478)


+ 0        gram  Nd_fcc_A1

       (750 C, 1 atm, S3, a=0.82354)


+ 0        gram  Nd_liquid

       (750 C, 1 atm, L1, a=0.72096)


+ 0        gram  NdZn_BCC_B2

       (750 C, 1 atm, S1, a=0.69774)
```

```
+ 0         gram  Nd_hcp_A3
          (750 C, 1 atm, S4, a=0.61384)

+ 0         gram  NaCl_Halite_(rock_salt_structure)
          (750 C, 1 atm, S1, a=0.53689)

+ 0         gram  NaCl_Halite_rocksalt_B1_cF8_(225)_Fm-3m
          (750 C, 1 atm, S1, a=0.53689)

+ 0         gram  ClNa_NaCl
          (750 C, 1 atm, S1, a=0.53689)

+ 0         gram  NaCl_liquid
          (750 C, 1 atm, L1, a=0.45972)

+ 0         gram  NaCl_liquid
          (750 C, 1 atm, L1, a=0.45972)

+ 0         gram  KCl_Sylvite_(NaCl_rock_salt_structure)
          (750 C, 1 atm, S1, a=0.42342)

+ 0         gram  KCl_Sylvite_rocksalt_B1_cF8_(225)_Fm-3m
          (750 C, 1 atm, S1, a=0.42342)

+ 0         gram  ClK_KCl
          (750 C, 1 atm, S1, a=0.40555)
```

```
+ 0        gram  KCl_liquid
         (750 C, 1 atm, L1, a=0.39815)

+ 0        gram  KCl_liquid
         (750 C, 1 atm, L1, a=0.39815)

+ 0        gram  KCl_B2_cP2_(221)_Pm-3m
         (750 C, 1 atm, S2, a=0.21725)

+ 0        gram  KCaCl3_perovskite_CaTiO3_cP5_(221)_Pm-3m
         (750 C, 1 atm, S3, a=7.3042E-02)

+ 0        gram  KCaCl3_prototype_KCuF3_tI20_(140)_I4/mcm
         (750 C, 1 atm, S2, a=6.8749E-02)

+ 0        gram  KCaCl3_Chlorocalcite_oP20_(62)_Pnma/Pbnm
         (750 C, 1 atm, S1, a=5.0601E-02)

+ 0        gram  NdZn2_CeCu2_oI12_Imma
         (750 C, 1 atm, S1, a=4.3821E-02)

+ 0        gram  CaCl2_prototype_TiO2_C4_tP6_(136)_P42/mn
         (750 C, 1 atm, S2, a=1.1037E-02)

+ 0        gram  CaCl2_prototype_CaCl2-C35_oP6_(58)_Pnnm
         (750 C, 1 atm, S1, a=1.1035E-02)
```

```
+ 0        gram  CaCl2_liquid
        (750 C, 1 atm, L1, a=1.0293E-02)

+ 0        gram  Zn_liquid
        (750 C, 1 atm, L1, a=1.2015E-03)

+ 0        gram  Na_liquid
        (750 C, 1 atm, L1, a=8.0805E-04)

+ 0        gram  Na_liquid
        (750 C, 1 atm, L1, a=8.0805E-04)

+ 0        gram  Na_liquid
        (750 C, 1 atm, L1, a=8.0805E-04)

+ 0        gram  Zn_hcp_Zn
        (750 C, 1 atm, S1, a=7.9288E-04)

+ 0        gram  Zn_bcc_A2
        (750 C, 1 atm, S4, a=7.6375E-04)

+ 0        gram  Zn_tetragonal_A6
        (750 C, 1 atm, S8, a=7.6375E-04)

+ 0        gram  Zn_bct_A5
        (750 C, 1 atm, S5, a=7.6375E-04)
```

+ 0 gram Zn_hcp_A3

(750 C, 1 atm, S2, a=6.7544E-04)

+ 0 gram Zn_fcc_A1

(750 C, 1 atm, S3, a=6.7544E-04)

+ 0 gram Zn_cbcc_A12

(750 C, 1 atm, S9, a=6.2677E-04)

+ 0 gram Na_bcc_A2

(750 C, 1 atm, S1, a=4.7132E-04)

+ 0 gram Na_bcc_A2

(750 C, 1 atm, S1, a=4.7132E-04)

+ 0 gram NdZn3_YZn3_oP16_Pmna

(750 C, 1 atm, S1, a=4.3269E-04)

+ 0 gram Na_fcc_A1

(750 C, 1 atm, S3, a=4.0548E-04)

+ 0 gram Na_fcc_A1

(750 C, 1 atm, S3, a=4.0548E-04)

+ 0 gram Na_hcp_A3

(750 C, 1 atm, S2, a=3.7511E-04)

```
+ 0        gram  Na_hcp_A3
        (750 C, 1 atm, S2, a=3.7511E-04)

+ 0        gram  Zn_rhombohedral_A7
        (750 C, 1 atm, S7, a=1.5174E-04)

+ 0        gram  K_liquid
        (750 C, 1 atm, L1, a=4.6363E-05)

+ 0        gram  K_liquid
        (750 C, 1 atm, L1, a=4.6363E-05)

+ 0        gram  K_bcc_A2
        (750 C, 1 atm, S1, a=2.6561E-05)

+ 0        gram  K_bcc_A2
        (750 C, 1 atm, S1, a=2.6561E-05)

+ 0        gram  K_fcc_A1
        (750 C, 1 atm, S3, a=2.2583E-05)

+ 0        gram  K_fcc_A1
        (750 C, 1 atm, S3, a=2.2583E-05)

+ 0        gram  Zn_diamond_A4
        (750 C, 1 atm, S6, a=2.1489E-05)
```

```
+ 0        gram  K_hcp_A3
         (750 C, 1 atm, S2, a=2.0760E-05)

+ 0        gram  K_hcp_A3
         (750 C, 1 atm, S2, a=2.0760E-05)

+ 0        gram  Ca_bcc_A2
         (750 C, 1 atm, S2, a=1.4801E-08)

+ 0        gram  Ca_bcc_A2
         (750 C, 1 atm, S2, a=1.4801E-08)

+ 0        gram  Ca_fcc_A1
         (750 C, 1 atm, S1, a=1.4178E-08)

+ 0        gram  Ca_fcc_A1
         (750 C, 1 atm, S1, a=1.4178E-08)

+ 0        gram  Ca_liquid
         (750 C, 1 atm, L1, a=1.3581E-08)

+ 0        gram  Ca_liquid
         (750 C, 1 atm, L1, a=1.3581E-08)

+ 0        gram  Ca_hcp_A3
         (750 C, 1 atm, S3, a=1.2289E-08)
```

```
+ 0        gram  NdZn5_CaCu5_hP6_P6/mmm
      (750 C, 1 atm, S1, a=1.0134E-08)

+ 0        gram  CaZn_B33_prototype_CrB_oC8_(63)_Cmcm
      (750 C, 1 atm, S1, a=4.5022E-10)

+ 0        gram  CaZn2_prototype_KHg2_oI12_(74)_Imma
      (750 C, 1 atm, S1, a=9.3270E-12)

+ 0        gram  Na2K_Laves_MgZn2_structure
      (750 C, 1 atm, S1, a=6.3966E-12)

+ 0        gram  Na2K_C14_prototype_MgZn2__hP12_(194)_P63
      (750 C, 1 atm, S1, a=6.3966E-12)

+ 0        gram  CaZn3_prototype_CaZn3_hP32_(194)_P63/mmc
      (750 C, 1 atm, S1, a=3.0931E-14)

+ 0        gram  K2ZnCl4_prototype_K2SO4_oP28_(62)_Pnma        T
      (750 C, 1 atm, S2, a=6.2334E-15)

+ 0        gram  Nd3Zn11_Al11La3_oI28_Immm
      (750 C, 1 atm, S1, a=5.8657E-15)

+ 0        gram  K2ZnCl4_oP84_(33)_Pna21                  T
      (750 C, 1 atm, S1, a=4.9466E-15)
```

```
+ 0         gram  Na2ZnCl4_prototype_K2SO4_oP28_(62)_Pnma          T
      (750 C, 1 atm, S1, a=3.0185E-16)

+ 0         gram  ZnCl2_liquid                                     T
      (750 C, 1 atm, L1, a=1.7936E-16)

+ 0         gram  ZnCl2_delta_oP12_(33)_Pna21                      T
      (750 C, 1 atm, S1, a=3.2056E-17)

+ 0         gram  CaZn5_D2d_prototype_CaCu5_hP6_(191)_P6/m
      (750 C, 1 atm, S1, a=2.8468E-19)

+ 0         gram  NdZn11_BaCd11_tI48_I41/amd
      (750 C, 1 atm, S1, a=3.2372E-24)

+ 0         gram  Ca3Zn_E1a_prototype_FeZr3_oC16_(63)_Cmcm
      (750 C, 1 atm, S1, a=1.1942E-25)

+ 0         gram  NdZn12_Mn12Th_tI26
      (750 C, 1 atm, S1, a=2.7079E-27)

+ 0         gram  KZn2Cl5_solid                                    T
      (750 C, 1 atm, S1, a=1.8821E-31)

+ 0         gram  Nd2Zn17_Ni17Th2_hP38
      (750 C, 1 atm, S1, a=3.7190E-33)
```

```
+ 0        gram  Nd2Zn17_Th2Zn17_hR19_R-3m
       (750 C, 1 atm, S2, a=1.8411E-33)

+ 0        gram  CaZn11_prototype_BaCd11_tI48_(141)_I41/a
       (750 C, 1 atm, S1, a=5.3961E-36)

+ 0        gram  Nd3Zn22_Pu3Zn22_tI100_I41/amd
       (750 C, 1 atm, S1, a=2.7580E-40)

+ 0        gram  CaZn13_D23_prototype_NaZn13_cF112_(226)_
       (750 C, 1 atm, S1, a=7.0340E-42)

+ 0        gram  NaZn13_D23_prototype_NaZn13_cF112_(226)_
       (750 C, 1 atm, S1, a=3.5896E-43)

+ 0        gram  Ca5Zn3_D81_prototype_Cr5B3_tI32_(140)_I4
       (750 C, 1 atm, S1, a=4.2182E-44)

+ 0        gram  KZn13_D23_prototype_NaZn13_cF112_(226)_F
       (750 C, 1 atm, S1, a=3.4539E-44)

+ 0        gram  K5Zn4Cl13_solid                    T
       (750 C, 1 atm, S1, a=2.9788E-63)

Cut-off limit for phase activities = 1.00E-70
```

```
  Data on 7 product species identified with "T" have been extrapolated outside their valid
temperature ranges


  *****************************************************************
    DELTA H      DELTA G      DELTA V      DELTA S     DELTA Cp
      (J)          (J)        (litre)       (J/K)        (J/K)
  *****************************************************************
   2.20115E+05  -2.48838E+05   0.00000E+00   4.58342E+02   9.62953E+01


  *****************************************************************
       H            G            V            S           Cp
      (J)          (J)        (litre)       (J/K)        (J/K)
  *****************************************************************
  -5.19744E+06  -7.83115E+06   0.00000E+00   2.57412E+03   1.04581E+03


                                  H            G            S           Cp
                                 (J)          (J)         (J/K)        (J/K)
  Salt-liquid#1              -5.18236E+06 -7.70816E+06  2.46865E+03  1.00274E+03
  Liquid#1                    1.65832E+04 -8.16827E+04  9.60424E+01  3.84176E+01
  NdCl3_solid                -3.16646E+04 -4.13124E+04  9.42942E+00  4.65886E+00


  Total mass/gram = 1057.1


  Databases: FTfrtz 8.0, FThall 8.0, FThelg 8.0, FTmisc 8.0, FTOxCN 8.0, FTpulp 8.0, FTsalt
8.0, FTox
  Data Search options: exclude gas ions; organic CxHy.. X(max) = 2; min soln cpts = 2
  Final conditions: T(C) = 750, P(atm) = 1
```

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                                   FactSage 8.0
 T = 750 C
 P = 1 atm
 V = 0 dm3


 STREAM CONSTITUENTS        AMOUNT/gram   TEMPERATURE/C   PRESSURE/atm
STREAM
 NdCl3_solid               1.7505E+02      750.00      1.0000E+00     1
 Zn_diamond_A4               1.2000E+01      750.00      1.0000E+00     1
 Ca_fcc_A1                 4.0000E+01      750.00      1.0000E+00     1
 NaCl_Halite_(rock_salt_s     3.6950E+02      750.00      1.0000E+00     1
 KCl_Sylvite_(NaCl_rock_s     4.6060E+02      750.00      1.0000E+00     1
 *****************************************************************
   Cp_INI       H_INI       S_INI       G_INI       V_INI
    J.K-1         J         J.K-1          J          dm3
 *****************************************************************
  9.49517E+02  -5.41755E+06   2.11578E+03  -7.58232E+06   0.00000E+00


                    EQUIL AMOUNT  MASS FRACTION    ACTIVITY
 PHASE: Salt-liquid#1(;#2)       gram
 NaCl                     3.6950E+02     3.9272E-01     4.5972E-01
 KCl                     4.6060E+02     4.8955E-01     3.9815E-01
 CaCl2                     1.1077E+02     1.1773E-01     1.0292E-02
 ZnCl2                    5.7961E-11     6.1604E-14     1.7936E-16
 TOTAL:                     9.4087E+02     1.0000E+00     1.0000E+00
```

```
  Site fraction of sublattice constituents:
  Na[+]                0.46837      Stoichiometry calculated
  K[+]                 0.45769
  Ca[2+]               7.3937E-02
  Zn[2+]               3.1506E-14
  -------------------------------------------------------------------
  Cl[-]                1.0000       Stoichiometry calculated
  System component        Amount/mol   Amount/gram   Mole fraction  Mass fraction
  Zn                  4.2529E-13    2.7805E-11    1.5191E-14    2.9553E-14
  Ca                  0.99805       40.000        3.5650E-02    4.2514E-02
  K                   6.1783        241.56        0.22069       0.25674
  Cl                  14.497        513.96        0.51783       0.54626
  Na                  6.3224        145.35        0.22584       0.15449
PHASE: Liquid#1(;#2)          gram      MASS FRACTION     ACTIVITY
Ca                    6.2206E-08    5.7612E-10    1.3582E-08
K                     2.8503E-08    2.6398E-10    4.6368E-05
Na                    4.3309E-07    4.0111E-09    8.0814E-04
Nd                    9.5974E+01    8.8886E-01    7.2104E-01
Zn                    1.2000E+01    1.1114E-01    1.2016E-03
TOTAL:                    1.0797E+02    1.0000E+00    1.0000E+00
  System component        Amount/mol   Amount/gram   Mole fraction  Mass fraction
  Nd                  0.66537       95.974        0.78379       0.88886
  Zn                  0.18354       12.000        0.21621       0.11114
  Ca                  1.5521E-09    6.2206E-08    1.8284E-09    5.7612E-10
  K                   7.2900E-10    2.8503E-08    8.5875E-10    2.6398E-10
  Na                  1.8839E-08    4.3309E-07    2.2191E-08    4.0111E-09
PHASE: BCC-A2#1;#2            gram      MASS FRACTION     ACTIVITY
```

```
Ca                     0.0000E+00     3.7010E-10     1.4802E-08
K                      0.0000E+00     2.5794E-11     2.6563E-05
Na                     0.0000E+00     5.4868E-10     4.7137E-04
Nd                     0.0000E+00     9.6582E-01     8.4487E-01
Zn                     0.0000E+00     3.4175E-02     7.6383E-04
TOTAL:                     0.0000E+00     1.0000E+00     9.3606E-01
PHASE: Salt-liquid2#1;#2         gram      MASS FRACTION     ACTIVITY
NaCl                     0.0000E+00     4.7245E-01     4.5972E-01
KCl                      0.0000E+00     5.2755E-01     3.9815E-01
TOTAL:                     0.0000E+00     1.0000E+00     9.1395E-01
PHASE: Liquid3                   gram      MASS FRACTION     ACTIVITY
KCl                      0.0000E+00     5.2714E-01     3.9815E-01
NaCl                     0.0000E+00     4.7286E-01     4.5972E-01
TOTAL:                     0.0000E+00     1.0000E+00     9.1342E-01
PHASE: DHCP-A3'                  gram      MASS FRACTION     ACTIVITY
Nd                     0.0000E+00     1.0000E+00     8.7349E-01
Ca                     0.0000E+00     3.2978E-11     1.2125E-09
TOTAL:                     0.0000E+00     1.0000E+00     8.7349E-01
PHASE: FCC-A1#1;#2               gram      MASS FRACTION     ACTIVITY
Ca                     0.0000E+00     1.5150E-10     1.4180E-08
K                      0.0000E+00     3.3964E-11     2.2585E-05
Na                     0.0000E+00     3.6147E-10     4.0552E-04
Zn                     0.0000E+00     3.7161E-04     6.7551E-04
Nd                     0.0000E+00     9.9963E-01     8.2363E-01
TOTAL:                     0.0000E+00     1.0000E+00     8.2430E-01
PHASE: Rocksalt#1;#2;#3          gram      MASS FRACTION     ACTIVITY
NaCl_halite                0.0000E+00     5.3699E-01     5.3690E-01
```

```
KCl_sylvite              0.0000E+00     4.6090E-01     4.2342E-01
CaCl[+]                  0.0000E+00     1.4358E-03     3.3840E-02
ZnCl[+]                  0.0000E+00     2.3768E-16     8.1489E-17
VaCl[-]                  0.0000E+00     6.7395E-04     4.7035E-03
TOTAL:                   0.0000E+00     1.0000E+00     7.2034E-01
PHASE: Fm3m#1;#2;#3            gram      MASS FRACTION     ACTIVITY
NaCl                     0.0000E+00     5.2660E-01     5.3689E-01
KCl                      0.0000E+00     4.7340E-01     4.2342E-01
TOTAL:                   0.0000E+00     1.0000E+00     7.1865E-01
PHASE: AlkCl-ss#1;#2;#3        gram      MASS FRACTION     ACTIVITY
NaCl                     0.0000E+00     5.2707E-01     5.3689E-01
KCl                      0.0000E+00     4.7293E-01     4.2342E-01
TOTAL:                   0.0000E+00     1.0000E+00     7.1792E-01
PHASE: HCP-A3#1;#2             gram      MASS FRACTION     ACTIVITY
Ca2Va                    0.0000E+00     4.7884E-11     2.0732E-16
K2Va                     0.0000E+00     4.1882E-11     4.3101E-10
Na2Va                    0.0000E+00     4.7692E-10     1.5819E-07
Zn2Va                    0.0000E+00     4.9850E-04     4.5626E-07
Nd2Va                    0.0000E+00     9.9950E-01     3.7684E-01
TOTAL:                   0.0000E+00     1.0000E+00     6.1455E-01
PHASE: cubic-Perovskite#1;#2   gram      MASS FRACTION     ACTIVITY
NaCaCl3                  0.0000E+00     4.9718E-08     5.0662E-04
KCaCl3_ht                0.0000E+00     1.0000E+00     7.3042E-02
TOTAL:                   0.0000E+00     1.0000E+00     7.3042E-02
PHASE: cubic-Perovskite#3      gram      MASS FRACTION     ACTIVITY
NaCaCl3                  0.0000E+00     9.9873E-01     5.0662E-04
KCaCl3_ht                0.0000E+00     1.2720E-03     7.3042E-02
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TOTAL:                    0.0000E+00    1.0000E+00    5.0720E-04

PHASE: ortho-Perovskite#1;#2    gram    MASS FRACTION    ACTIVITY

NaCaCl3                   0.0000E+00    7.1767E-08    5.0662E-04

KCaCl3_lt                 0.0000E+00    1.0000E+00    5.0602E-02

TOTAL:                    0.0000E+00    1.0000E+00    5.0602E-02

PHASE: ortho-Perovskite#3      gram    MASS FRACTION    ACTIVITY

NaCaCl3                   0.0000E+00    9.9913E-01    5.0662E-04

KCaCl3_lt                 0.0000E+00    8.7408E-04    5.0602E-02

TOTAL:                    0.0000E+00    1.0000E+00    5.0702E-04

PHASE: C42#1;#2                gram    MASS FRACTION    ACTIVITY

NdZn2                     0.0000E+00    1.0000E+00    4.3826E-02

CaZn2                     0.0000E+00    1.3222E-10    9.3280E-12

TOTAL:                    0.0000E+00    1.0000E+00    4.3826E-02

PHASE: Rutile#1;#2;#3          gram    MASS FRACTION    ACTIVITY

CaCl2_beta                0.0000E+00    1.0000E+00    1.1037E-02

ZnCl2                     0.0000E+00    2.6078E-17    2.3438E-19

TOTAL:                    0.0000E+00    1.0000E+00    1.1037E-02

PHASE: Zn-liq                  gram    MASS FRACTION    ACTIVITY

Zn                        0.0000E+00    9.8643E-01    1.2181E-03

Na                        0.0000E+00    1.3568E-02    8.1767E-04

TOTAL:                    0.0000E+00    1.0000E+00    1.2573E-03

PHASE: HCP-Zn#1;#2             gram    MASS FRACTION    ACTIVITY

Ca                        0.0000E+00    5.8172E-06    1.1209E-08

Na                        0.0000E+00    7.2559E-02    3.7261E-04

Zn                        0.0000E+00    9.2744E-01    7.9296E-04

TOTAL:                    0.0000E+00    1.0000E+00    9.3239E-04

PHASE: Liquid2                 gram    MASS FRACTION    ACTIVITY
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Ca                      0.0000E+00     1.0825E-06     1.3581E-08
Na                      0.0000E+00     1.0000E+00     8.0805E-04
TOTAL:                      0.0000E+00     1.0000E+00     8.0806E-04
PHASE: Liquid-Alloy#1;#2         gram      MASS FRACTION     ACTIVITY
Ca                      0.0000E+00     1.0825E-06     1.3581E-08
Na                      0.0000E+00     1.0000E+00     8.0805E-04
TOTAL:                      0.0000E+00     1.0000E+00     8.0806E-04
PHASE: Na-K(BCC)#1;#2           gram      MASS FRACTION     ACTIVITY
Na                      0.0000E+00     9.7896E-01     4.7132E-04
K                      0.0000E+00     2.1043E-02     2.6561E-05
TOTAL:                      0.0000E+00     1.0000E+00     4.7708E-04
PHASE: BCC#1;#2                gram      MASS FRACTION     ACTIVITY
Ca                      0.0000E+00     5.8724E-06     1.4801E-08
Na                      0.0000E+00     9.9999E-01     4.7132E-04
TOTAL:                      0.0000E+00     1.0000E+00     4.7132E-04
PHASE: FCC                   gram      MASS FRACTION     ACTIVITY
Ca                      0.0000E+00     1.7079E-07     1.4178E-08
Na                      0.0000E+00     1.0000E+00     4.0548E-04
TOTAL:                      0.0000E+00     1.0000E+00     4.0548E-04
PHASE: D03#1;#2                gram      MASS FRACTION     ACTIVITY
Zn3Nd                     0.0000E+00     9.9909E-01     9.9064E-05
Na3Nd                     0.0000E+00     8.5208E-04     2.5004E-13
K3Nd                     0.0000E+00     5.8901E-05     4.4749E-17
TOTAL:                      0.0000E+00     1.0000E+00     9.9492E-05
PHASE: D2d#1;#2                gram      MASS FRACTION     ACTIVITY
NdZn5                     0.0000E+00     1.0000E+00     1.0276E-08
CaZn5                     0.0000E+00     2.1581E-11     2.8470E-19
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TOTAL:                    0.0000E+00     1.0000E+00     1.0276E-08

PHASE: D81                     gram      MASS FRACTION     ACTIVITY

Nd5Zn3                    0.0000E+00     1.0000E+00     4.9539E-12

Ca5Zn3                    0.0000E+00     1.6664E-07     4.2186E-44

TOTAL:                    0.0000E+00     1.0000E+00     4.9539E-12

PHASE: beta-K2SO4#1             gram      MASS FRACTION     ACTIVITY

Na2ZnCl4                  0.0000E+00     5.4386E-04     2.9452E-16

K2ZnCl4-ht                0.0000E+00     9.9946E-01     6.2335E-15

TOTAL:                    0.0000E+00     1.0000E+00     6.2411E-15

PHASE: beta-K2SO4#2             gram      MASS FRACTION     ACTIVITY

Na2ZnCl4                  0.0000E+00     9.8293E-01     2.9452E-16

K2ZnCl4-ht                0.0000E+00     1.7070E-02     6.2335E-15

TOTAL:                    0.0000E+00     1.0000E+00     3.0284E-16

PHASE: tI48                    gram      MASS FRACTION     ACTIVITY

NdZn11                    0.0000E+00     1.0000E+00     3.2376E-24

CaZn11                    0.0000E+00     1.4658E-12     5.3967E-36

TOTAL:                    0.0000E+00     1.0000E+00     3.2376E-24

PHASE: hP38                    gram      MASS FRACTION     ACTIVITY

Ca2Zn17                   0.0000E+00     8.1382E-21     3.4000E-73

Nd2Zn17                   0.0000E+00     1.0000E+00     3.7193E-33

TOTAL:                    0.0000E+00     1.0000E+00     3.7193E-33

PHASE: D23#1;#2                gram      MASS FRACTION     ACTIVITY

NaZnZn4Zn4Zn4             0.0000E+00     4.7661E-02     3.5899E-43

CaZnZn4Zn4Zn4             0.0000E+00     9.5234E-01     7.0355E-42

TOTAL:                    0.0000E+00     1.0000E+00     7.3945E-42

                          gram                ACTIVITY

NdCl3_solid(s)            8.3078E+00          1.0000E+00
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NdCl3_liquid(liq)           0.0000E+00                  9.5065E-01

Nd_dhcp(s)                  0.0000E+00                  8.7340E-01

Nd_bcc_A2(s2)               0.0000E+00                  8.4478E-01

Nd_fcc_A1(s3)               0.0000E+00                  8.2354E-01

Nd_liquid(liq)              0.0000E+00                  7.2096E-01

NdZn_BCC_B2(s)              0.0000E+00                  6.9774E-01

Nd_hcp_A3(s4)               0.0000E+00                  6.1384E-01

NaCl_Halite_(rock_sal(s)      0.0000E+00                  5.3689E-01

NaCl_Halite_rocksalt_(s)      0.0000E+00                  5.3689E-01

ClNa_NaCl(s)                0.0000E+00                  5.3689E-01

NaCl_liquid(liq)            0.0000E+00                  4.5972E-01

NaCl_liquid(liq)            0.0000E+00                  4.5972E-01

KCl_Sylvite_(NaCl_roc(s)      0.0000E+00                  4.2342E-01

KCl_Sylvite_rocksalt_(s)      0.0000E+00                  4.2342E-01

ClK_KCl(s)                  0.0000E+00                  4.0555E-01

KCl_liquid(liq)             0.0000E+00                  3.9815E-01

KCl_liquid(liq)             0.0000E+00                  3.9815E-01

KCl_B2_cP2_(221)_Pm-(s2)      0.0000E+00                  2.1725E-01

KCaCl3_perovskite_Ca(s3)      0.0000E+00                  7.3042E-02

KCaCl3_prototype_KCu(s2)      0.0000E+00                  6.8749E-02

KCaCl3_Chlorocalcite_(s)      0.0000E+00                  5.0601E-02

NdZn2_CeCu2_oI12_Imma(s)      0.0000E+00                  4.3821E-02

CaCl2_prototype_TiO2(s2)      0.0000E+00                  1.1037E-02

CaCl2_prototype_CaCl2(s)      0.0000E+00                  1.1035E-02

CaCl2_liquid(liq)           0.0000E+00                  1.0293E-02

Zn_liquid(liq)              0.0000E+00                  1.2015E-03

Na_liquid(liq)              0.0000E+00                  8.0805E-04
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Na_liquid(liq)	0.0000E+00	8.0805E-04
Na_liquid(liq)	0.0000E+00	8.0805E-04
Zn_hcp_Zn(s)	0.0000E+00	7.9288E-04
Zn_bcc_A2(s4)	0.0000E+00	7.6375E-04
Zn_tetragonal_A6(s8)	0.0000E+00	7.6375E-04
Zn_bct_A5(s5)	0.0000E+00	7.6375E-04
Zn_hcp_A3(s2)	0.0000E+00	6.7544E-04
Zn_fcc_A1(s3)	0.0000E+00	6.7544E-04
Zn_cbcc_A12(s9)	0.0000E+00	6.2677E-04
Na_bcc_A2(s)	0.0000E+00	4.7132E-04
Na_bcc_A2(s)	0.0000E+00	4.7132E-04
NdZn3_YZn3_oP16_Pmna(s)	0.0000E+00	4.3269E-04
Na_fcc_A1(s3)	0.0000E+00	4.0548E-04
Na_fcc_A1(s3)	0.0000E+00	4.0548E-04
Na_hcp_A3(s2)	0.0000E+00	3.7511E-04
Na_hcp_A3(s2)	0.0000E+00	3.7511E-04
Zn_rhombohedral_A7(s7)	0.0000E+00	1.5174E-04
K_liquid(liq)	0.0000E+00	4.6363E-05
K_liquid(liq)	0.0000E+00	4.6363E-05
K_bcc_A2(s)	0.0000E+00	2.6561E-05
K_bcc_A2(s)	0.0000E+00	2.6561E-05
K_fcc_A1(s3)	0.0000E+00	2.2583E-05
K_fcc_A1(s3)	0.0000E+00	2.2583E-05
Zn_diamond_A4(s6)	0.0000E+00	2.1489E-05
K_hcp_A3(s2)	0.0000E+00	2.0760E-05
K_hcp_A3(s2)	0.0000E+00	2.0760E-05
Ca_bcc_A2(s2)	0.0000E+00	1.4801E-08

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Ca_bcc_A2(s2)                 0.0000E+00          1.4801E-08
Ca_fcc_A1(s)                  0.0000E+00          1.4178E-08
Ca_fcc_A1(s)                  0.0000E+00          1.4178E-08
Ca_liquid(liq)                0.0000E+00          1.3581E-08
Ca_liquid(liq)                0.0000E+00          1.3581E-08
Ca_hcp_A3(s3)                 0.0000E+00          1.2289E-08
NdZn5_CaCu5_hP6_P6/mm(s)      0.0000E+00          1.0134E-08
CaZn_B33_prototype_Cr(s)      0.0000E+00          4.5022E-10
CaZn2_prototype_KHg2_(s)      0.0000E+00          9.3270E-12
Na2K_Laves_MgZn2_stru(s)      0.0000E+00          6.3966E-12
Na2K_C14_prototype_Mg(s)      0.0000E+00          6.3966E-12
CaZn3_prototype_CaZn3(s)      0.0000E+00          3.0931E-14
K2ZnCl4_prototype_K2(s2) T    0.0000E+00          6.2334E-15
Nd3Zn11_Al11La3_oI28_(s)      0.0000E+00          5.8657E-15
K2ZnCl4_oP84_(33)_Pna(s) T    0.0000E+00          4.9466E-15
Na2ZnCl4_prototype_K2(s) T    0.0000E+00          3.0185E-16
ZnCl2_liquid(liq)        T    0.0000E+00          1.7936E-16
ZnCl2_delta_oP12_(33)(s) T    0.0000E+00          3.2056E-17
CaZn5_D2d_prototype_C(s)      0.0000E+00          2.8468E-19
NdZn11_BaCd11_tI48_I4(s)      0.0000E+00          3.2372E-24
Ca3Zn_E1a_prototype_F(s)      0.0000E+00          1.1942E-25
NdZn12_Mn12Th_tI26(s)         0.0000E+00          2.7079E-27
KZn2Cl5_solid(s)         T    0.0000E+00          1.8821E-31
Nd2Zn17_Ni17Th2_hP38(s)       0.0000E+00          3.7190E-33
Nd2Zn17_Th2Zn17_hR19(s2)      0.0000E+00          1.8411E-33
CaZn11_prototype_BaCd(s)      0.0000E+00          5.3961E-36
Nd3Zn22_Pu3Zn22_tI100(s)      0.0000E+00          2.7580E-40
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CaZn13_D23_prototype_(s)     0.0000E+00            7.0340E-42

NaZn13_D23_prototype_(s)     0.0000E+00            3.5896E-43

Ca5Zn3_D81_prototype_(s)     0.0000E+00            4.2182E-44

KZn13_D23_prototype_N(s)     0.0000E+00            3.4539E-44

K5Zn4Cl13_solid(s)      T   0.0000E+00            2.9788E-63

*******************************************************************

 DELTA Cp      DELTA H      DELTA S      DELTA G      DELTA V

  J.K-1          J          J.K-1          J          dm3

*******************************************************************

 9.62953E+01   2.20115E+05   4.58342E+02  -2.48838E+05   0.00000E+00


*******************************************************************

   Cp            H            S            G            V

  J.K-1          J          J.K-1          J          dm3

*******************************************************************

 1.04581E+03  -5.19744E+06   2.57412E+03  -7.83115E+06   0.00000E+00


                  Cp          H           S           G

                 J.K-1        J         J.K-1         J

Salt-liquid#1         1.00274E+03 -5.18236E+06  2.46865E+03 -7.70816E+06

Liquid#1              3.84176E+01  1.65832E+04  9.60424E+01 -8.16827E+04

NdCl3_solid(s)        4.65886E+00 -3.16646E+04  9.42942E+00 -4.13124E+04


Cut-off limit for phase activities = 1.00E-70


Data on 7 product species identified with "T" have been extrapolated outside their valid
temperature ranges
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Databases: FTfrtz 8.0, FThall 8.0, FThelg 8.0, FTmisc 8.0, FTOxCN 8.0, FTpulp 8.0, FTsalt 8.0, FTox

Data Search options: exclude gas ions; organic CxHy.. X(max) = 2; min soln cpts = 2

Final conditions: T(C) = 750, P(atm) = 1