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Iowa State College

Edwin H. Olson
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SEPARATION OF CERIUM FROM OTHER RARE EARTHS

BY IGNITION OF THE NITRATES

Russell W. Johnson and Edwin H. Olson

September 1958

Ames Laboratory
at
Iowa State College
F. H. Spedding, Director
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Separation of Cerium from Other Rare Earths by Ignition of the Nitrates

Russell W. Johnson and Edwin H. Olson

ABSTRACT

Cerium was separated from the light rare earths by ignition of the nitrates whereby the cerous nitrate was decomposed to ceric oxide. Small scale investigations were made using sodium nitrate and magnesium nitrate hexahydrate as fluxes. A cost estimate based on data from the small scale investigations showed the sodium nitrate ignition to be more economical; therefore, bench scale investigations were made using sodium nitrate. With a weight ratio of sodium nitrate to rare earth nitrate hexahydrate of 1:2 and a temperature of approximately 295°C for 12 to 16 hours, a nearly quantitative conversion of cerous nitrate to ceric oxide was obtained. The ceric oxide obtained upon dissolving the soluble sodium nitrate and undecomposed rare earth nitrates and filtering, using "Celite" filtering aid as a precoat, was found to be quite pure. Indications are that an even purer ceric oxide could possibly be obtained if a lower temperature for a longer length of time had been used.

INTRODUCTION

If the present high costs of the purified rare earths could be reduced to a more practical level, many new uses of the rare
earths would probably be developed by industry. For a great many years, the rare earths were separated by the very tedious fractional crystallization method. The Ames Laboratory has devoted considerable time and effort toward the separation of a rare earth mixture into its individual components. Spedding, et al,\(^{(1,2,3,4)}\)


have prepared the pure individual rare earths from a mixture by means of the ion exchange method. Although ion exchange is the current method of preparing pure individual rare earths, it is slow and also costly. Bochinski, Smutz, and Spedding\(^{(5)}\) have demonstrated that the rare earths can be separated by liquid-liquid extraction, a process which shows promise of being a more rapid method of producing fairly pure individual rare earths.

A mixture of rare earth nitrates, obtained as by-products from the production of thorium from monazite sands, was used in the studies by Bochinski, Smutz, and Spedding. Their studies show that the absence of cerium would simplify the separation and purification of the remaining individual rare earths. Also, since cerium makes up approximately one-half of the monazite rare earth mixture, its prior removal would greatly reduce the bulk of material to be processed. At the same time, the cost of separating and purifying the individual rare earths by an extraction process would be reduced.

For many years it has been known that cerous nitrate will decompose to ceric oxide at a lower temperature than the other rare earth nitrates. Debray (6) separated cerium by igniting at 300-350°C a mixture containing eight to ten parts by weight of potassium nitrate per part of rare earth nitrate mixture, followed by a water leach.

Dennis and Magee (7) objected to Debray's method. They pointed out that cerous nitrate decomposes at 200°C, and a mixture of praseodymium and neodymium nitrates decomposes at 300°C. Since the temperature at which the investigations were carried out was in
the region of 325°C, the ceric oxide must have contained some praseodymium and neodymium oxides. Dennis and Magee carried out ignitions with an equimolecular mixture of potassium and sodium nitrates which melts at 231°C. At 320°C and above they found praseodymium and neodymium oxides in the residue although all the cerous nitrate was not completely decomposed. At 300°C they obtained quite pure ceric oxide, but found that if thorium or the yttrium earths (elements 64 to 71) were present in the original mixture these elements would be found in the ceric oxide fraction.

Marsh(8) studied the oxide precipitation of the rare earths by nitrate ignition. He pointed out that the crystal structures of the oxides have a marked effect on separation. Since praseodymium and neodymium oxides are capable of forming a solid solution with the cubic ceric oxide, these elements are the ones most likely to contaminate the ceric oxide. Lanthanum oxide, which has a hexagonal structure, on the other hand does not appear to have much capacity for assuming the cubic structure of ceric oxide. Therefore, lanthanum oxide is less likely to be found with the ceric oxide.

The present authors felt it advisable to investigate further the possibility of separating cerium from the other rare earths by ignition of the nitrates. Instead of using potassium nitrate or

an equimolecular mixture of sodium and potassium nitrates, ignitions were made using sodium nitrate or magnesium nitrate hexahydrate as fluxes. Processes employing the two salts were compared. The two main variables studied were the temperature and time required for complete conversion of the cerous nitrate to ceric oxide. A third variable studied was the weight ratio of the salt to rare earth nitrate. Also, various methods by which the ceric oxide could be separated from the undecomposed rare earth nitrates were investigated.

Experimental

Materials - Lindsay Chemical Company Code 350 rare earth nitrates were used. A typical analysis shows 46.6 percent cerium, 5.6 percent praseodymium, 19.0 percent neodymium, 2.4 percent samarium, and 26.4 percent lanthanum, expressed as oxides. For the small scale investigations, reagent grade sodium nitrate and magnesium nitrate hexahydrate were used. Some of the bench scale investigations with sodium nitrate were made with reagent grade materials. The other bench scale investigations were made with a technical grade sodium nitrate obtained from McKesson and Robbins, Inc. A typical analysis by the Nitrogen Division, Allied Chemical and Dye Corporation is shown in Table I. The bench scale investigations with magnesium nitrate hexahydrate were made with reagent grade materials. "Celite" analytical filter aid was obtained from the Johns-Manville Company. All other chemicals used were reagent grade.
Table I.

Typical Analysis of "Arcadian" Nitrate of Soda

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage (dry basis)</th>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Nitrogen</td>
<td>16.42%</td>
<td>NaCl</td>
<td>0.23%</td>
</tr>
<tr>
<td>NaNO₃ (dry basis)</td>
<td>99.63%</td>
<td>Sulfates as Na₂SO₄</td>
<td>0.17%</td>
</tr>
<tr>
<td>Insoluble</td>
<td>0.004%</td>
<td>Calcium as CaO</td>
<td>0.061%</td>
</tr>
<tr>
<td>Moisture</td>
<td>0.41%</td>
<td>Magnesia as MgO</td>
<td>0.003%</td>
</tr>
<tr>
<td>NaNO₂</td>
<td>0.009%</td>
<td>Iron as Fe₂O₃</td>
<td>0.001%</td>
</tr>
<tr>
<td>Alkalinity as Na₂O</td>
<td>0.006%</td>
<td>Alumina as Al₂O₃</td>
<td>0.002%</td>
</tr>
</tbody>
</table>

Equipment - A constant temperature bath, with a eutectic mixture of lithium, potassium, and sodium nitrates as the heating media, was constructed for the small scale investigations. The eutectic mixture contained 53 percent by weight potassium nitrate, 30 percent lithium nitrate, and 17 percent sodium nitrate and had a melting point of 128°C. The salt bath was contained in a porcelainized iron kettle nine inches high and eleven inches in diameter. The kettle, wrapped with a double layer of asbestos and glass wool for insulation, was set on a 660-watt hot plate, seven inches in diameter. Fire brick insulation surrounded the hot plate which was the major source of heat. A 16-ohm resistance heating coil was immersed in the fused salt bath to supply the additional heat needed. The resistance coil, connected to a powerstat (7.5 amps; 110 volts), was enclosed
in a pyrex glass tube nine inches long and one inch in diameter. The fused salt eutectic was circulated by means of an electric stirrer and a glass stirring rod to maintain a uniform temperature. A thermometer, enclosed in a pyrex glass tube, was immersed in the fused salt bath. The bath temperature was controlled by adjusting the power input to the heating coil. The reactants were placed in 38 x 200-millimeter test tubes which were inserted into the bath.

For the bench scale investigations 4 x 15 inch pyrex glass tubes closed at one end were used. Although the tubes were longer than necessary, the extra length gave a safety factor in case of spattering of the contents during heating. One pound of sodium nitrate and two pounds of rare earth nitrate hexahydrate were used. The heating source for the bench scale studies was a four-inch-diameter electrical resistance furnace with an overall length of 12 inches. The furnace was designed for a current capacity of four to five amperes at 110 volts. The furnace temperature was measured with a chromel-alumel thermocouple. The power input to the furnace was controlled by a powerstat, and the current was measured with an ammeter.

Procedure - For the preliminary investigations, weighed quantities of rare earth nitrate hexahydrate and magnesium nitrate hexahydrate or sodium nitrate were mixed and placed in several 38 x 200 millimeter test tubes. The test tubes were all placed in a constant temperature
bath at the same time. At various time intervals individual tubes were removed and cooled to room temperature.

In the bench scale operations, weighed quantities of rare earth nitrate hexahydrate and magnesium nitrate hexahydrate were mixed and placed in a 4 x 15 inch pyrex tube which was then inserted into the resistance heated furnace. The furnace was preheated in a few of the runs, but most of them were made starting with a cold furnace which was then heated to the desired operating temperature. Samples were withdrawn at various time intervals by inserting into the mixture a 10 millimeter glass tube which served as a pipette.

Analyses - The samples from both the preliminary and bench scale operations were prepared for analysis using the following procedure:

1. The samples were leached with either water or a two percent nitric acid solution to dissolve the undecomposed rare earth nitrates.
2. The leach-slurry was filtered using "celite" as a filter aid to separate the insoluble ceric oxide from the soluble rare earth nitrates.
3. The ceric oxide was dissolved using a nitric acid-hydrogen peroxide solution and the celite removed by filtration. The cerium was precipitated from the filtrate as the oxalate using oxalic acid; the oxalate was filtered and ignited back to ceric oxide. This ceric oxide was then analyzed spectrographically to determine the amounts of other rare earth nitrates that had decomposed to the oxides.
(4) The filtrate from step (2) was qualitatively analyzed for cerium by treating a portion with ammonium hydroxide and hydrogen peroxide. The development of a yellow colored precipitate, referred to as a positive test, indicated the presence of cerium. The minimum amount of cerium detectable by the qualitative test was approximately 3000 ppm. If the qualitative test for cerium was negative, the filtrate was treated with oxalic acid to precipitate all of the rare earths as oxalates. The oxalate precipitate was filtered and ignited to the oxide which was then analyzed for ppm cerium by the Analytical Group of this Laboratory.

Preliminary Investigations

The purpose of the preliminary investigations was to determine the optimum processing conditions for the separation of cerium when small amounts of rare earth nitrates were used for the ignition. The ignition variables primarily studied were the nitrate salt to be used as a flux, the weight ratio of the nitrate salt to rare earth nitrate hexahydrate, temperature, and the time required for the conversion of cerous nitrate to ceric oxide.

When the rare earth nitrate hexahydrates are ignited without any other nitrate salt present, they melt and the water vaporizes. After most of the water has been removed, cerous nitrate will start to decompose to ceric oxide. This decomposition will continue until all of the materials have solidified. The conversion
of cerous nitrate to ceric oxide is far from complete at this time. The decomposition will continue, but it is very slow because the gases are trapped within the solid materials.

Previous investigators have found that the addition of either potassium nitrate or a eutectic mixture of potassium and sodium nitrates as fluxes will keep the materials fluid, thus allowing the decomposition to proceed at a faster rate. The present authors felt that the use of alternate fluxes should be investigated. Fusions were made using sodium nitrate, potassium nitrate, ferric nitrate, cupric nitrate, ammonium nitrate, aluminum nitrate, zinc nitrate and magnesium nitrate. The usual commercial form was used in each case. Some of these salts were investigated for use as oxidizing agents rather than as fluxes. It was thought that by igniting the mixtures near the decomposition temperature of the salt, cerous nitrate would possibly be oxidized to the ceric salt without the formation of ceric oxide.

Ferric nitrate and cupric nitrate definitely showed no promise. They decomposed to either the oxide or hydrated oxide. Ammonium nitrate decomposed too rapidly, and there was the danger of detonation. Potassium nitrate would not be used alone because of the great length of time required for the ignition, but could be used in a eutectic mixture with sodium nitrate. However, the cost of potassium nitrate prevents its use in a eutectic mixture.
Zinc nitrate showed some promise but it had the disadvantage of forming the hydrated oxide. Aluminum nitrate also decomposed to the hydrated oxide at elevated temperatures. It was interesting to note, however, that at 175°C some of the cerium(III) nitrate was converted to cerium(IV) nitrate. Of the nitrates studied, the two that showed the most promise were sodium nitrate and magnesium nitrate.

Three different methods for the removal of ceric oxide from the undecomposed rare earth nitrates were investigated. The first method was designed primarily to permit the removal of magnesium or sodium nitrate salt flux from the ceric oxide and undecomposed rare earth nitrates in the reaction slug. This method involved extracting the undecomposed rare earth nitrates into a 50-50 mixture of tributyl phosphate and benzene, followed by leaching the magnesium nitrate from the ceric oxide with water. It was difficult to obtain intimate contacting and complete removal of the undecomposed rare earth nitrates because of the formation of a gummy residue after the second contact of the ground slug with the tributyl phosphate-benzene extractant. This residue also retained some of the extractant which, after water-leaching to remove the magnesium nitrate, resulted in a holdup of ceric oxide at the interface.

The second method for removing the cerium after ignition was to dissolve the ignition mixture in nitric acid to give a cerium(IV)
nitrate solution. Since cerium(IV) nitrate is much more extractable into tributylphosphate than the other rare earths, the cerium could be separated by liquid-liquid extraction. Upon trying the method, cerium(III) was always found to be present in the aqueous phase after extraction. Since reduction of a small amount of the cerium must take place either during the dissolution step or the extraction step, this method was also discarded.

The third method involved leaching the materials with either water or two percent nitric acid and then filtering. The filtration step proved to be difficult due to the small particle size of the ceric oxide. However, much of the difficulty was eliminated by using a precoat of "Celite". This was the method finally used.

When the samples containing magnesium nitrate hexahydrate were inserted into the salt bath, the mixture melted and the water which was combined with the nitrate salts evaporated vigorously. At times, it was thought the materials would be expelled from the test tubes. After the water had evaporated, nitrogen dioxide fumes began to evolve. When the conversion of cerous nitrate to ceric oxide was complete or nearly so, practically no nitrogen dioxide fumes were noticed.

The samples containing sodium nitrate behaved generally in the same manner. However, it was uncertain whether or not the mixture melted completely prior to the evolution of the water vapor. In bench scale studies it was indicated that probably
not all of the materials melted. Also, the evolution of nitrogen dioxide was slower when sodium nitrate was used. One characteristic of the ignitions with sodium nitrate was that the ceric oxide settled out. This was not noticed in the ignitions using magnesium nitrate hexahydrate.

The optimum conditions found for the conversion of cerous nitrate to ceric oxide are shown in Table II, where the analyses are tabulated for cerium in the rare earth oxides obtained from the undecomposed rare earth nitrates. For both sodium nitrate and magnesium nitrate hexahydrate, the weight ratio of salt to rare earth nitrate hexahydrate could not be reduced below 1:2. When lower ratios were used, the materials solidified and showed no signs of remelting. The primary purpose of the sodium nitrate or magnesium nitrate hexahydrate was to serve as a flux. For sodium nitrate, the reaction time was shortened when a 1:2 ratio was used instead of a 1:1. Since the ignition with magnesium nitrate hexahydrate took place so rapidly at 275°C when a 1:1 salt ratio was used, it was considered inadvisable to use higher temperatures. When the salt ratio was changed to 1:2 for the ignitions with magnesium nitrate hexahydrate, the reaction time at a temperature of 275°C was approximately six times greater. Since sodium nitrate melts at a higher temperature than magnesium nitrate hexahydrate, its use required a higher temperature for ignition.
Table II
Analyses for Cerium in the Rare Earth Oxides Obtained from the Undecomposed Rare Earth Nitrates from the Preliminary Investigations

<table>
<thead>
<tr>
<th>Ignition</th>
<th>Salt</th>
<th>Weight Ratio (Salt: Re(NO₃)₃·6H₂O)</th>
<th>Temperature (°C)</th>
<th>Time (hours)</th>
<th>%CeO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Mg(NO₃)₂·6H₂O</td>
<td>1:1</td>
<td>225</td>
<td>12</td>
<td>*</td>
</tr>
<tr>
<td>B</td>
<td>&quot;</td>
<td>&quot;</td>
<td>250</td>
<td>6</td>
<td>0.14</td>
</tr>
<tr>
<td>C</td>
<td>&quot;</td>
<td>&quot;</td>
<td>275</td>
<td>1</td>
<td>0.05</td>
</tr>
<tr>
<td>D</td>
<td>NaN₃</td>
<td>1:2</td>
<td>295</td>
<td>24</td>
<td>0.26</td>
</tr>
</tbody>
</table>

* No quantitative analysis.

Also, the reaction time required was much longer. The reason for this increased time is discussed under "Bench Scale Investigations". Temperatures higher than 300°C were not used because neodymium and praseodymium nitrates would decompose.

Table III shows the purity of the ceric oxide obtained. Usually the highest impurity was neodymium. There was no quantitative test available for samarium in the ceric oxide; however, spectrographic qualitative tests showed very little to be present.
Table III
Spectrographic Analyses for the Other Rare Earths in the Ceric Oxide Obtained from the Preliminary Investigations

<table>
<thead>
<tr>
<th>Ignition</th>
<th>Salt</th>
<th>Temperature (°C)</th>
<th>La$_2$O$_3$ (%)</th>
<th>Pr$<em>6$O$</em>{11}$ (%)</th>
<th>Nd$_2$O$_3$ (%)</th>
<th>Sm$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Mg(NO$_3$)$_2$·6$\text{H}_2$O</td>
<td>225</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>—</td>
</tr>
<tr>
<td>B</td>
<td>&quot;</td>
<td>250</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>0.10</td>
<td>FT</td>
</tr>
<tr>
<td>C</td>
<td>&quot;</td>
<td>275</td>
<td>0.08</td>
<td>&lt;0.05</td>
<td>0.08</td>
<td>T</td>
</tr>
<tr>
<td>D</td>
<td>NaNO$_3$</td>
<td>295</td>
<td>0.05</td>
<td>&lt;0.05</td>
<td>0.08</td>
<td>FT</td>
</tr>
</tbody>
</table>

T = trace
FT = faint trace
dash = not detected

At the time the preliminary investigations were completed, the results from the quantitative analyses for cerium were not available. Therefore, the bench scale investigations were started on the basis of the results from the qualitative tests.

Bench Scale Investigations

A cost estimate for ignitions using magnesium nitrate hexahydrate and sodium nitrate, based on data from the preliminary investigations, indicated that sodium nitrate would be more
economical. The magnesium nitrate would cost approximately 29¢/lb and the sodium nitrate approximately 2¢/lb. Even with the extra cost of heating required when using sodium nitrate and without recovering it, the cost estimate indicated that the total processing cost would be less than the cost of recovering the expensive magnesium nitrate hexahydrate for reuse. Therefore, most of the bench scale investigations were made using sodium nitrate.

In small scale ignitions using magnesium nitrate hexahydrate, the ceric oxide did not settle out as it did when sodium nitrate was used. However, in the bench scale investigations using magnesium nitrate, the ceric oxide could be settled, but only after allowing the charge to stand for a considerable length of time. A closer control of temperature to maintain a more fluid charge might have permitted faster settling.

Other difficulties encountered with the use of magnesium nitrate hexahydrate were hydrolysis and subsequent decomposition at higher temperatures and the fact that the cooled charge adhered to the walls of the glass reaction tube. The dissolution of the soluble magnesium and rare earth nitrates caused swelling which resulted in breakage of the glass reaction tubes. In the case of sodium nitrate ignitions, the cooled charge shrunk away from the walls of the glass reaction tube and could be removed as a slug. The sodium nitrate was also noted to be quite stable at the temperatures used in these investigations.
Preliminary investigations showed 24 hours at 295°C was required to approach a complete conversion of cerous nitrate to ceric oxide when a 1:2 weight ratio of sodium nitrate to rare earth nitrate hexahydrate was used. Bench scale operations with a 1:2 weight ratio of sodium nitrate to rare earth nitrate hexahydrate has shown nearly complete conversion in 12-16 hours at 295-300°C. The increase in surface area for nitrogen dioxide evolution probably helped to decrease the time required. Also, the increase in air convection currents in the larger reaction tube helped remove the nitrogen dioxide faster, thus allowing the reaction to proceed at a faster rate.

The bench scale investigations furnished information on how the ignitions could best be handled. To prevent water vapors from forcing partially dissolved or molten materials upward in the reaction tube, it was found necessary to mix the rare earth nitrate hexahydrates and sodium nitrate at least 12 hours prior to ignition and to start with a cold furnace to permit a smooth, uniform evolution of water from the charge.

The first few ignitions were made starting with a preheated furnace. The rapid evolution of the water vapors forced the viscous charge upwards in the reaction tube. Stirring was necessary to prevent the charge from being forced out of the tube, but was undesirable because after the water had all been
evolved the charge crystallized and did not remelt until its temperature reached approximately 275°C. Since the evolution of water vapors proceeded much less vigorously at the lower temperatures, it was decided to start with a cold furnace and let the temperature rise gradually. This helped to reduce the difficulty but did not eliminate it completely.

As was mentioned previously, the removal of the waters of crystallization by heating proceeded much more smoothly when the reactants were mixed at least 12 hours prior to ignition. After standing, the mixture appeared very moist; in fact, the bottom portion was almost fluid. However, there was no increase in weight due to absorbed water from the atmosphere. Analysis revealed the rare earth nitrate hexahydrates did not contain any excess water. The sodium nitrate, which had been stored in an open bag, did not appear to be hygroscopic. One possible explanation is that a surface reaction was taking place between the rare earth nitrate hexahydrates and the sodium nitrate, whereby a double salt was formed. The double salt, \( \text{Re(NO}_3\text{)}_3 \cdot 2\text{NaNO}_3 \cdot 4\text{H}_2\text{O} \), would require less waters of crystallization than the rare earth nitrate hexahydrate. Therefore, the water that was released would partially dissolve the rare earth nitrates and sodium nitrate. When the mixture is heated, this water would be available for dissolving more of the salts. This dissolution apparently was
the reason for the increased ease of water evolution from the charge. When the sodium nitrate and rare earth nitrate hexahydrates were mixed and immediately placed in the furnace, this dissolution did not take place. When the mixture was heated, the water was released directly as vapors. Further evidence of this lack of dissolution was the grainy appearance of the stirring rod upon removal from the viscous molten charge.

In the discussion of the preliminary investigations, it was mentioned there was uncertainty as to whether or not all of the charge had melted prior to the evolution of the water vapors. From the bench scale investigations, it was noted that most of the charge melted or dissolved. However, in the larger scale operations, it was found that there was a solidification step which had not been noticed with the smaller samples. The charge solidified at about 133°C. Between 270°C and 280°C the charge began to remelt at the edges, and the cerous nitrate began to decompose.

When an ignition was considered to be complete, the reaction tube was removed from the furnace and the charge allowed to cool to room temperature. While cooling and solidifying, the charge contracted and it could be removed from the reaction tube in the form of a slug. Figure 1 shows a typical slug. The light-colored portion of the slug is the ceric oxide which settled out. The ceric oxide has a canary-yellow color. The upper portion, which is violet in color, consists of the undecomposed rare earths.
Figure 1. Photograph of a Typical Cooled Slug After Ignition of One Pound of Sodium Nitrate and Two Pounds of Rare Earth Nitrate Hexahydrate at 295°C.
Table IV shows the distribution of ceric oxide and the undecomposed rare earth nitrates in a slug. Samples of the upper and lower phases were taken for the analyses.

Table IV
Distribution of Ceric Oxide and the Undecomposed Rare Earth Nitrates in a Slug from the Ignition of a 1:2 Weight Ratio of Sodium Nitrate to Rare Earth Nitrate Hexahydrate at 295°C

<table>
<thead>
<tr>
<th>Component</th>
<th>Lower Phase</th>
<th>Upper Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re$_2$O$_3$*</td>
<td>5.9 g</td>
<td>27.3 g</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>20.8 g</td>
<td>0.06 g</td>
</tr>
</tbody>
</table>

* Undecomposed rare earth nitrates, reported as rare earth oxides (Re$_2$O$_3$).

After determining the best ignition procedure and conditions, several ignitions were made to determine the minimum time required to convert the cerous nitrate to ceric oxide. Table V shows the results of the analyses for cerium in the undecomposed rare earth nitrates. These analyses were used to determine whether or not the reaction was complete. The temperatures given are those of the charge inside the glass reaction tube. By inserting a
Table V
Analyses for Cerium in the Rare Earth Oxides from the Undecomposed Rare Earth Nitrates for Ignitions Made Using a 1:2 Weight Ratio of Sodium Nitrate to Rare Earth Nitrate Hexahydrate

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Time (hours)</th>
<th>%CeO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>5/12</td>
<td>295 ± 3</td>
<td>12</td>
<td>0.031</td>
</tr>
<tr>
<td>5/13</td>
<td>295 ± 3</td>
<td>12</td>
<td>0.021</td>
</tr>
<tr>
<td>5/14</td>
<td>290 ± 3</td>
<td>10</td>
<td>4.27</td>
</tr>
<tr>
<td>6/24</td>
<td>295 ± 3</td>
<td>8</td>
<td>0.079</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14</td>
<td>0.017</td>
</tr>
<tr>
<td>6/26</td>
<td>295 ± 3</td>
<td>12</td>
<td>0.253</td>
</tr>
</tbody>
</table>

thermometer into the molten charge, a temperature drop across the glass wall of about 20°C was found. Therefore, the outside wall temperature was maintained at about 315°C for most of the ignitions. The ignition of sample 5/14 was intentionally stopped prior to complete conversion of the cerous nitrate to ceric oxide to find out how the filtration of the ceric oxide would be affected. The rare earth nitrate hexahydrates for 6/24 and 6/26 were from different lots. This gives some indication of how the ignition conditions might vary with different lots. The ignition of sample
6/24 was made with rare earth nitrates which had been heated at 110°C for two days. The same sample gives some idea of the time required to convert the last portion of the cerous nitrate to ceric oxide.

Table VI shows the purity of ceric oxide obtained from the ignitions shown in Table V. Sample 5/14 indicates that the use of a lower temperature for a longer period of time might result in a higher purity ceric oxide. Neodymium was found to be the greatest impurity, which was not surprising since at 295-300°C neodymium nitrate starts to decompose. Analyses showed that only faint traces of samarium and sodium were present.

Table VI
Spectrographic Analyses for Rare Earths in Ceric Oxide Obtained from Ignitions Made using a 1:2 Weight Ratio of Sodium Nitrate to Rare Earth Nitrate Hexahydrate

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Time (hours)</th>
<th>%Nd₂O₃</th>
<th>%Pr₆O₁₁</th>
<th>%La₂O₃</th>
</tr>
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<tbody>
<tr>
<td>5/12</td>
<td>295 ± 3</td>
<td>12</td>
<td>0.3</td>
<td>&lt; 0.05</td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td>5/13</td>
<td>295 ± 3</td>
<td>12</td>
<td>0.3</td>
<td>&lt; 0.05</td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td>5/14</td>
<td>290 ± 3</td>
<td>10</td>
<td>&lt; 0.02</td>
<td>&lt; 0.02</td>
<td>&lt; 0.02</td>
</tr>
<tr>
<td>6/24</td>
<td>295 ± 3</td>
<td>14</td>
<td>0.5</td>
<td>&lt; 0.05</td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td>6/26</td>
<td>295 ± 3</td>
<td>12</td>
<td>0.1</td>
<td>&lt; 0.05</td>
<td>&lt; 0.05</td>
</tr>
</tbody>
</table>
Filtration Studies

While making the small scale investigations the ceric oxide particles obtained after dissolving the soluble rare earth nitrates were found to be colloidal. A filtration was made using Schleicher and Schuell Red Ribbon Filter Paper Number 589, but the ceric oxide particles were not retained. The Schleicher and Schuell Company makes only two or three filter papers more retentive, but it is doubtful that even these would have held the ceric oxide. This problem was eliminated by using "Celite" filter aid.

In many industrial processes, the most costly operation is filtration. Therefore, bench scale filtration studies were made to ascertain the difficulties which might be encountered.

The filtration tests were made using an Eimco filter test leaf with an area of approximately 0.1 sq. ft. The apparatus and procedure were similar to that shown by Perry(9). All of the tests were made at constant pressures. A precoat of "Celite" was applied prior to the filtration of the ceric oxide. The equations given by Brown(10) were utilized to determine the filtration constant, $C_v$.


and the resistance due to the filter cloth and precoat of "Celite", expressed as an equivalent volume of filtrate, $V_e$.

Table VII shows the results of the filtration tests. Although the table does not show all of the filtration test results, the constants obtained for the other tests were of the same magnitude as those in Table VII. Except for the two high values of 26.3 and 14.3 for the 5/8 and 5/14 samples, the filtration constants, $C_v$, agree quite well. It was noted during the ignition step that the ceric oxide did not settle as fast for the 5/8 sample as it did for the 5/6 sample, perhaps because the ignition temperature was slightly lower. The 5/14 sample was also ignited at a slightly lower temperature and was stopped before the conversion of cerous nitrate to ceric oxide was complete. These factors, plus the high concentrations and viscosities, may have caused the high values for $C_v$. The filtration of the 5/2 and 5/5 samples showed that as the thickness of "Celite" increased the value of $C_v$ decreased.

The values of $V_e$ are much higher than were expected. The "Celite" was not expected to increase $V_e$ this much. For most filtrations, the resistance due to the filter media is small with the controlling resistance being that of the cake. However, the high values of $V_e$ obtained in these filtration tests show the resistance due to the "Celite" coating can not be neglected in filter capacity calculations.
Table VII
Filtration Test Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration* gRe₂O₃/100 ml</th>
<th>Viscosity centipoises</th>
<th>&quot;Celite&quot;</th>
<th>CeO₂</th>
<th>AP</th>
<th>Cᵥx10³ lb/sec-ft²/cm⁶</th>
<th>Ve cm³</th>
</tr>
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<tbody>
<tr>
<td>5/2</td>
<td>10.19</td>
<td>5.3</td>
<td>&lt;1/32</td>
<td>5/32</td>
<td>2.02x10³</td>
<td>8.06</td>
<td>307</td>
</tr>
<tr>
<td>5/2</td>
<td>&quot;</td>
<td>&quot;</td>
<td>3/16</td>
<td>3/32</td>
<td></td>
<td>5.43</td>
<td>585</td>
</tr>
<tr>
<td>5/5</td>
<td>11.54</td>
<td>6.1</td>
<td>3/32</td>
<td>5/32</td>
<td>2.04x10³</td>
<td>7.89</td>
<td>500</td>
</tr>
<tr>
<td>5/5</td>
<td>&quot;</td>
<td>&quot;</td>
<td>9/32</td>
<td>1/8</td>
<td>2.04x10³</td>
<td>7.89</td>
<td>500</td>
</tr>
<tr>
<td>5/8</td>
<td>16.28</td>
<td>8.0</td>
<td>1/8</td>
<td>3/16</td>
<td></td>
<td>8.73</td>
<td>755</td>
</tr>
<tr>
<td>5/8</td>
<td>16.86</td>
<td>8.0</td>
<td>1/4</td>
<td>1/8</td>
<td>2.05x10³</td>
<td>26.3</td>
<td>382</td>
</tr>
<tr>
<td>5/12</td>
<td>13.13</td>
<td>7.0</td>
<td>5/32</td>
<td>1/8</td>
<td>2.04x10³</td>
<td>5.81</td>
<td>480</td>
</tr>
<tr>
<td>5/13</td>
<td>14.83</td>
<td>7.5</td>
<td>7/32</td>
<td>1/8</td>
<td></td>
<td>7.04</td>
<td>709</td>
</tr>
<tr>
<td>5/14</td>
<td>18.72</td>
<td>8.6</td>
<td>5/32</td>
<td>5/32</td>
<td></td>
<td>14.3</td>
<td>369</td>
</tr>
<tr>
<td>6/5</td>
<td>—</td>
<td>—</td>
<td>1/4</td>
<td>5/32</td>
<td></td>
<td>7.76</td>
<td>629</td>
</tr>
<tr>
<td>6/6</td>
<td>—</td>
<td>—</td>
<td>1/4</td>
<td>1/8</td>
<td></td>
<td>7.63</td>
<td>518</td>
</tr>
</tbody>
</table>

* Concentration of undecomposed rare earth nitrates as rare earth oxides, Re₂O₃.
Filtration tests at different pressures were made to determine whether or not the ceric oxide cake was compressible. The data according to treatment by Brown\textsuperscript{(10)} showed it to be incompressible. The ceric oxide cake was very easily peeled from the "Celite" after most of the wash solution was withdrawn and the pressure released.

The data show the filtration to be difficult. However, due to the ease by which the ceric oxide layer was separated from the "Celite", it is felt the filtration could be readily adapted to a rotary filter by using a "Celite" precoat.

Discussion

It has been demonstrated by small bench scale studies that cerous nitrate in a rare earth nitrate mixture can be decomposed to a quite pure ceric oxide by ignition of a mixture of rare earth nitrates, using either sodium nitrate or magnesium nitrate as fluxes. Due to the higher cost and the processing difficulties encountered using magnesium nitrate, sodium nitrate was the preferred flux, even though longer ignition times were required. Although this ignition processing method does not give as pure a cerium compound as does the ion exchange method, it is a more rapid method and the volume of materials to be handled is much smaller. The cerium purity obtained by this method would probably be about the same as that obtained by liquid-liquid extraction; however, here the volume of materials to be handled is again much smaller.
Based upon the bench scale results of this investigation, a storage period is recommended after the mixing of the sodium and rare earth nitrates to permit a more uniform and less vigorous release of the waters of hydration. It was theorized that a surface reaction between the sodium nitrate and rare earth nitrate hexahydrate resulted in the formation of a double salt and simultaneous release of water which then partially dissolved the salts. When the temperature was raised during ignition, the water was evaporated from a saturated solution instead of being vigorously released as a vapor from the solid salts at higher temperatures.

Actual optimum conditions were not established for the sodium nitrate ignitions. It was found, however, that ignition at approximately 295°C for 12 to 16 hours resulted in a nearly quantitative removal of cerium from a rare earth nitrate mixture as a quite pure ceric oxide. Indications are that lower temperatures and longer ignition times would probably result in a higher purity ceric oxide.

Filtration tests made on water slurries of the ceric oxide-undecomposed rare earth nitrates showed that the very fine ceric oxide particles were difficult but not impossible to filter. A precoat of "Celite" was found necessary to permit satisfactory filtration. No difficulty was encountered in washing the soluble sodium and rare earth nitrates from the filter cake. Tests made at different pressures indicated that the ceric oxide cake was
incompressible. It was also noted that the ceric oxide cake could be easily peeled away from the "Celite" precoat, indicating that a continuous rotary filter with a "Celite" precoat could be satisfactorily used.

Figure 2 shows a flow sheet for a proposed process. One possible way to reduce the filtration load would be to remove the solidified reaction mass from the reaction vessel and separate the settled ceric oxide portion from the low-cerium content sodium nitrate-rare earth nitrate phase. The ceric oxide rich portion could then be leached with a much smaller volume of water which would reduce considerably the volume of slurry to be filtered. The remainder of the reaction mass would be leached, and the small amount of ceric oxide removed by sedimentation.

Since the nitrate salts are fluid in the final ignition step and the ceric oxide settles out, the ignition might possibly be adapted to a continuous process. The upper and lower phases could be tapped as more sodium nitrate and rare earth nitrate hexahydrate are added. This would mean that two leaching steps would be required. A clarification or sedimentation step would be required for separation of ceric oxide from the rare earth and sodium nitrates in the upper phase. The filtration step required for the ceric oxide-rich lower phase would still be necessary. However, such a continuous flow process would
Figure 2. Proposed Flow Sheet for the Separation of Cerium from the Rare Earth Nitrates.
reduce the filtration load and speed up the processing of the
undecomposed rare earth nitrates.

This ignition process shows promise as a method for the
preparation of a quite pure ceric oxide. This method might also
be advantageous in removing the cerium prior to the removal of
the other rare earths by solvent extraction or ion exchange
methods, since with the cerium removed, the volumes of solutions
to be processed would be reduced by approximately 50 percent.