[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

OBSERVATIONS ON THE RARE EARTHS. XXVIII. THE SEPARATION OF CERIUM

BY J. W. NECKERS[1] WITH H. C. KREMERS

RECEIVED AUGUST 19, 1927 PUBLISHED APRIL 5, 1928

The separation methods applied to cerium are quite different from those usually applied to the rare earths. Cerium when oxidized to the quadrivalent state assumes properties sufficiently different from the other trivalent earths to effect a quantitative separation.

The oldest method using this property is that of Mosander[2] who used chlorine or bromine to oxidize the cerium. Other methods are the neutral permanganate process proposed by Stapff[3] and perfected by Roberts,[4] and the neutral potassium bromate method proposed by James.[5] From the standpoint of the preparation of cerium free from other earths or the complete removal of cerium from the other earths, the first method is inefficient due to the necessity of several successive treatments with chlorine, making the process slow. The neutral permanganate method is rapid but does not yield pure cerium. The cerium dioxide precipitates along with the manganese dioxide, giving a very bulky precipitate which carries down with it considerable quantities of other rare earths. The potassium bromate method yields pure cerium but is very slow and expensive; long-continued boiling and excess of reagent are necessary.

One method of oxidation reported to be quite rapid is electrolytic oxidation. Knorre[6] reported the oxidation of cerous sulfate by ammonium persulfate with the precipitation of a basic sulfate. Consequently, oxidation of cerous sulfate anodically might lead to the precipitation of ceric cerium due to the formation of persulfate around the anode. Bricout[7] also reports the precipitation of ceric dichromate by the electrolysis of a slightly acid solution of cerous chromate. These two reports and others give a possibility of a cerium separation by anodic oxidation.

Experimental

(1) Anodic Oxidation.—Solutions of cerium earths containing 30% of cerous cerium were electrolyzed using graphite electrodes. Electrolysis of the nitrates, chlorides and sulfates of the above solutions in

---

[1] This paper represents part of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate School of the University of Illinois.

[2] Mosander, *Ann.*, **48**, 210 (1843).

[3] Stapff, *J. prakt. Chem.*, [1] **79**, 258 (1860).

[4] Roberts, *Am. J. Sci.*, [5] **31**, 350 (1911).

[5] James, THIS JOURNAL, **33**, 1326 (1911); **34**, 757 (1912).

[6] Knorre, *Z. angew. Chem.*, **10**, 717 (1897).

[7] Bricout, *Compt. rend.*, **118**, 146 (1894).

the presence of a slight excess of the corresponding acids gave deep red colorations, indicating oxidation of cerium but no precipitation. Prolonged boiling during electrolysis failed to hydrolyze the ceric cerium.

(2) **Precipitation of Ceric Phosphate.**—It is evident from the above results that ceric cerium can only be removed from an acid solution by the addition of an ion which will form an insoluble ceric salt. Cerium, in its tetravalent state, is very similar to zirconium and hafnium; in fact, it so characteristically resembles Sub-Group A of Group Four in the periodic table that cerium occupied the position now held by hafnium until the discovery of the latter. The phosphates of these quadrivalent metals are very insoluble. The addition of orthophosphoric acid or any of its salts causes immediate precipitation of ceric phosphate. The other rare earth phosphates are soluble in dilute mineral acids. Knorre[6] and others have reported ceric phosphates for the purpose of analysis.

Ignited cerium group oxides were dissolved in concentrated nitric acid and diluted to make a 10% solution. Ignition of the oxides caused 90% of the cerium to be oxidized to the ceric state. This solution was heated to 80° and sodium phosphate solution slowly added. All of the ceric cerium was precipitated as phosphate in a heavy, flocculent form which settled well. The presence of 5% of free nitric acid prevented the precipitation of any of the other earths.

This ceric phosphate filtered well and could be washed free from the other earths. The filtrate was further treated with excess sodium phosphate and potassium permanganate slowly added. The cerous cerium still present was thus completely oxidized and removed as phosphate. Analysis of the filtrate showed the presence of less than 0.02% of cerium. The presence of this small amount of cerium is due to the slight solubility of the phosphate in nitric acid.

A 5% nitrate solution of the cerium group earths was then prepared having present 5% of free nitric acid and a slight excess of sodium phosphate. This solution was electrolyzed as described above. Ceric phosphate was thrown down as anodic oxidation took place. After prolonged electrolysis it was found that approximately 1% of cerous cerium remained in solution. This was evidently due to cathodic reduction. In another trial the cathode was surrounded by a porous cup. In a short time the cathode became coated with a gelatinous precipitate of ceric phosphate and electrolysis ceased. This method was then abandoned.

Ceric phosphate is a heavy, cream colored precipitate when thrown down from a hot solution with constant stirring. It is sparingly soluble in 5 *N* nitric acid. Very little solubility is indicated in nitric acid of less than 2.5 *N*. Ceric phosphate is very quickly decomposed with strong sodium hydroxide solution giving insoluble ceric hydroxide. This hydroxide filters well, can readily be dissolved in nitric acid and cerous oxalate precipitated from this solution by the addition of oxalic acid. A suspension of ceric phosphate in mineral acids may also be reduced to cerous phosphate by oxalic acid.

The above method was next tried on a large-scale laboratory or semicommercial basis. Some two hundred kilos of commercial cerium group earths were treated in the following manner. The hydroxides were ignited in order to convert as much as possible of the cerium into the ceric state. A 10% nitrate solution of these oxides in the presence of 5% of free nitric acid was treated in 60-liter evaporation dishes. Phosphate precipitation was carried out at a temperature of 80°, aided by mechanical stirring. Permanganate was then added until oxidation and precipitation of ceric phosphate were complete. The cerium free earths were precipitated from the hot filtrate as oxalates, utilizing the 5% of nitric acid present as optimum condition for oxalate precipitation. The ceric phosphate after thorough washing was treated with 50% caustic soda solution in an iron vessel. The ceric hydroxide was washed free from sodium phosphates, dissolved in nitric acid and the oxalate precipitated out.

It seemed possible that this phosphate method might also be used to separate the cerium and thorium together from cerium group earths. Monazite sand was accordingly "cracked" with concentrated sulfuric acid, the excess acid fumed off and the thorium and cerium earth sulfates were dissolved in water. The solution after acidifying with a little sulfuric acid was treated with potassium permanganate. Both thorium and ceric phosphates were precipitated together. The phosphate ion of the original monazite is thus utilized. To gain complete precipitation it was necessary to add a little more sodium phosphate.

Thus it is possible, where it is not of special interest to remove thorium separately, to obtain directly from monazite sand rare earths which have been freed of thorium and cerium by one precipitation.

(3) Discussion of Results

Anodic oxidation of cerium in sulfate and nitrate solutions goes to about 90% completion with no precipitation. Addition of an ion, such as the phosphate, allows 99% oxidation and precipitation of the cerium. If other oxidation methods are used, such as the addition of potassium permanganate, the cerium is entirely removed. The obvious reason for this complete separation is the immediate removal of the ceric cerium as an insoluble substance as soon as it reaches the ceric state. There is undoubtedly an equilibrium between the cerous and ceric states during an oxidation process. In other methods used this equilibrium is shifted mostly by excess reagents or heating, both of which require considerable time as well as reagents. In this method, however, such means are not necessary, for the presence of the phosphate causes immediate precipitation of ceric cerium as fast as it is formed. In this way the equilibrium is shifted practically completely toward the ceric ion, which is forthwith precipitated, giving complete separation.

The precipitation and removal of cerium in the form of ceric phosphate, as described in this research, has several practical points worthy of consideration. In both the chlorine and potassium bromate methods at least two treatments are necessary for the complete removal of cerium, especially in large quantities. The neutral permanganate method is slow, bulky and gives a precipitate which is difficult to filter and causes much occlusion of the filtrate. Several days are required for complete reaction and a large quantity of potassium permanganate is necessary. In both the bromate and permanganate methods the excess acid which is present after dissolving the rare earths must be neutralized with calcium carbonate before the oxidation can be applied. For precipitation of the filtrate as oxalate, acid must again be added.

The phosphate method described gives 100% removal of cerium in one precipitation and is rapid. It takes a minimum of expensive oxidizing agents and the same acid concentration employed in the removal of cerium is that required for the precipitation of remaining earths as oxalates, saving time for neutralization as well as reagents. The use of the permanganate in acid solution also increases the efficiency. The neutral permanganate is only three-fifths as efficient as that used in the acid phosphate method. Also, in the acid solution, manganese dioxide is not formed in quantities to prove troublesome as in the neutral method.

It is undoubtedly possible to use other oxidizing agents for oxidizing the cerium to the tetravalent form for precipitation. It is also possible to remove thorium, zirconium and cerium completely, in one step, in the purification of rare earth ores. This should eliminate considerable time, as well as loss of rare earths and reagents, and prove a very efficient method.

Summary

Ninety per cent. oxidation may be accomplished anodically when applied to cerous sulfate or nitrate. Ceric chloride tends to decompose to cerous chloride and chlorine, so anodic oxidation is inefficient in this case. Separation of cerium is best accomplished by precipitation of a ceric compound. Addition of a soluble phosphate to a slightly acid solution of ceric nitrate causes the complete precipitation of the cerium as ceric phosphate. The other rare earth phosphates are soluble in the dilute acid. Thorium phosphate is also precipitated. Thus rare earths may be obtained free from cerium and thorium in one precipitation.

URBANA, ILLINOIS