# THE SEPARATION OF OLD YTTERBIUM FROM GADOLINITE.

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In 1902, Dennis and Dales published a paper on Yttrium group separations (Journal of Amer. Chem. Soc. Vol. 24, No. 5, May, 1902). In this paper was presented one method which was shown to offer unusually rapid separation of the members of the yttrium group. Hardly enough material (Yttrium group oxides from sypilite) was at hand to permit of making a very extensive study of the most interesting fraction, which is the last one. The process referred to (reference page 430) is the one there called Fractionation with Ammonium Carbonate and dilute Acetic Acid. It is my purpose to show that nearly pure ytterbium oxide can be obtained from gadolinite by this method with comparatively few fractionations, and also to gain an idea of the approximate quantity of ytterbium oxide which can be thus obtained.

## Preparation of Material.

The material used in these experiments was Gadolinite, partly because it was available and partly because it was the mineral from which Ytterbium was originally obtained. Twelve pounds of the solid dark Gadolinite was first crushed and ground to a fine powder in order to get it into a form in which it could be easily digested. The powdered material was put into large sized porcelain evaporating dishes, enough being taken to fill each dish half full. Enough Aqua Regia was then added to cover the powdered mass. The mineral was then stirred well and evaporated on air bath, nearly to dryness. Con. hydrochloric acid was added and the mass evaporated down again. The treatment with con. hydrochloric acid was repeated until no trace of chlorine was indicated when tested by the starch and potassium iodide paper method.

During the first evaporation to dryness a solid cement-like mass formed which was very slow in dissolving and was treated separately with Aqua Regia and afterwards with Con. hydrochloric acid. Continued application of this method with heat resulted in its all being broken up.

When all the material was freed from chlorine the mass was covered with con. hydrochloric acid, heated about an hour, stirred, and the whole poured into a large cylinder. Enough water and hydrochloric acid (one-half each) was added to double the volume. This was all well stirred and allowed to stand several hours for the solid part to settle. The silica settled quickly, but the silt and greenish mass (probably iron silicate) settled very slowly and formed a distinct layer on the surface of the silica. The acid solution contained a part of the rare earths of the yttrium and cerium groups; also glucinum and iron and some other impurities.

After settling quite clear the acid solution was siphoned off and just neutralized with ammonium hydroxide. A permanent brownish precipitate showed when the solution was slightly alkaline. Just enough acid was added to dissolve this precipitate. Then 25cc excess of the acid was added for 5 liters of solution, which made about the correct per cent of acidity for precipitation of the earths present. This solution was then set away while other extractions were made on the same residue. About half of the rare earths present in the gadolinite ore were extracted by the first aqua regia treatment. The process of extraction was repeated six times with profit. When these extractions were completed and the resulting solutions made slightly acid as above, the cerium and yttrium groups of earths were precipitated by adding an excess of solid oxalic acid and stirring with air. The solution required about three hours of this treatment to get complete precipitation. The oxalate precipitates settled readily to the bottom.

The supernatant liquid was siphoned off from the above. This solution contained iron and glucinum as they do not form precipitates with oxalic acid in dilute acid solutions. If too much hydrochloric acid is added before treating with oxalic acid, some of the cerium and yttrium group oxalates may not precipitate completely, as some are slightly soluble in dilute acid solutions. To be sure that all of the cerium and yttrium oxalates were all precipitated the solution was partially neutralized with ammonium hydroxide and treated again with oxalic acid crystals. No glucinum will precipitate as long as the solution is acid with oxalic acid or hydrochloric acid. Some cerium and yttrium groups of earths were recovered by this treatment. When all the cerium and yttrium earths were removed, the glucinum and iron were precipitated from the solution by adding an excess of ammonium hydroxide. This precipitate was saved on account of the glucinum which it contained. The remaining solution was discarded as it contained only ammonium salts and some impurities.

The white oxalates secured as described above were washed a number of times in large cylinders by siphonation with distilled water. They were finally washed in a Buchner funnel with distilled water using strong linen fibre filter papers.

The oxalates were removed on the filter paper to an air bath, heated at a temperature of 105 degrees C. or higher until thoroughly dry. This required several hours. A temperature of 140 degrees C. did no harm to the precipitate. Heat may be applied until the paper begins to char. Too great a temperature would partially convert the oxalates into oxides and make the mass hard to dissolve later.

The oxalates were then powdered very fine in a mortar and ignited in small quantities in a quartz evaporator. The powder must be stirred all the time in order to prevent the lower portion from becoming over-heated. A light gray color indicates that the oxalates have been converted into carbonates, which is the form desired. Too much heat will convert the carbonates to oxides, which because of the cerium present makes it hard to dissolve. On the other hand, if not heated enough, the oxalates will not be destroyed. If a small amount of oxalate precipitate is left over it will be destroyed later by nitric acid.

The carbonates of the earths secured as described above were then treated with concentrated nitric acid and hydrogen peroxide. One liter of concentrated nitric acid was put in a large porcelain evaporating dish, heat applied and the earths added as long as they would dissolve. (1.5 kgm of Carbonate for 1 liter of nitric acid.) About 50cc of hydrogen peroxide was added to put the last of it in solution. Several hours time with heat was required to dissolve the carbonates. The solution with a slight trace of sediment was then put into large cylinders and allowed to settle two days. Some of the sediment dissolved in that time. The material left on the bottom of the cylinder then was mostly carbon and oxides that were difficultly soluble (probably mostly cerium di-oxide). This strong acid solution was filtered through a double filter in a Buchner funnel. The solution was then neutralized with ammonium hydroxide. Acid and alkali were added slowly to get the exact neutral point. The solution was stirred continuously with air to aid in getting this result. Two days' time was allowed for this treatment to be certain of the neutral point. When exactly neutral, the solution was subjected to the alkaline sulphate treatment for the removal of the cerium group. An excess of sulphate was added and stirred for two days to get complete reaction. Time seemed to be a factor in getting this reaction. One treatment with alkaline sulphate was not sufficient to remove all of the cerium group. In fact, seven treatments were necessary before the absorption spectra of old didymium disappeared. The alkaline sulphate used was mostly potassium sulphate, but some sodium sulphate was used. After each sulphate treatment the earths had to be precipitated and washed free from sulphate. The precipitation and washing of the hydroxides was tried, but was found to be too tedious. The precipitation of the earths as oxalates was found to be the most satisfactory. The oxalate precipitate was washed free from sulphate, filtered on a Buchner funnel and dried in an air bath. The oxalates were then powdered, roasted to carbonate and the carbonates dissolved in nitric acid. After the above described treatments the solution then left was supposed to contain only yttrium group elements.

### Fractionations.

When the last treatment was finished the yttrium group earths were left dissolved in nitric acid. The earths were precipitated from this solution by ammonium hydroxide and washed. These hydroxides were dissolved in saturated ammonium carbonate solution. The high atomic weight material dissolves very readily. That of lower atomic weight dissolves more difficultly and cerium and didymium hydroxides if present remain largely undissolved. I found that the ammonium carbonate solution would dissolve more earths if it had some ammonia water added to it (1 to 10). This was doubtless due to the presence in the solution of carbamate or other carbon compounds from the solid ammonium carbonate used. The best results were obtained by adding the earth hydroxides in small quantities to the ammonium carbonate solution and stirring until the solution was saturated. When the ammonium carbonate solution was poured onto the earth hydroxides a much larger quantity of ammonium carbonate was required to effect solution, as a sort of coating was formed over the mass of hydroxides which would not readily dissolve. The excess of earths remaining in each jar after the solution was saturated, was filtered off. This would not dissolve readily in ammonium carbonate so it was dissolved in nitric acid, reprecipitated with ammonia and then dissolved in fresh ammonium carbonate solution.

After all the earths were dissolved in saturated ammonium carbonate they were fractioned with acetic acid solution. First the ammonium carbonate solution of the earths was treated with concentrated acetic acid to destroy the excess of ammonium carbonate present. The acid had to be added slowly and the mixture stirred well on account of bubbling. The appearance of a very faint cloud indicated the end point. In working with a sample of the solution it was found necessary to give considerable time to this treatment because when the acid was added rapidly to a cloud a large precipitate would fall on standing several minutes. After bringing the whole solution to a faint cloud a sample of it was tried with different quantities of one-thirtieth strength acetic acid solution (1 acid to 29 water) to determine what proportion of this strength acid was necessary to obtain maximum precipitation. At this point Dennis and Dales used the amount of one-thirtieth acetic acid solution necessary each time to give maximum precipitation. This gave from 4 to 6 fractionations, but the last one, while the most interesting, was very small. In an effort to increase the amount of this last fraction without impairing the efficiency of the fractionation, I used a quantity of one-thirtieth strength acetic acid less than that required for maximum precipitation. In the first part of the work one-fifth the amount of one-thirtieth strength acetic acid necessary for maximum precipitation was used. This amount was estimated in the following way:

### Example.

18 tubes—10 cc each (clouded as described above).
Added 1 cc of 1-30 acet. to 1st tube.
Added 2 cc of 1-30 acet. to 2nd tube.
Added 3 cc of 1-30 acet. to 3rd tube.
Added 4 cc of 1-30 acet. to 4th tube, etc.

I found the maximum precipitation in the 15th tube. Thus 15cc of one-thirtieth strength acetic acid in 10cc of sample gave maximum precipitation. I used one-fifth that amount or 3cc of one-thirtieth strength acetic acid for each 10cc of sample. This was added slowly to prevent too rapid bubbling. A granular precipitate slowly settled to the bottom forming the first fraction. This was filtered off. On trial it was found that this same amount of acetic acid would not produce a precipitate in the remaining solution, but that it was necessary to bring the solution to a cloud again. After determining the amount necessary then for maximum precipitation in the clouded solution, it was treated in the same way with one-fifth that amount. The precipitate thus formed was filtered off and was known as fraction number two.

The ammonium acetate then in the solution prevented further fractions from being properly extracted from this solution, because the earths are readily soluble in ammonium acetate. The remaining carbonate present was destroyed with nitric acid and the earths removed from the solution by precipitating with ammonium hydroxide.

The earth hydroxides were filtered in the Buchner filter and again dissolved in saturated ammonium carbonate solution. The ammonium carbonate solution was again brought to a faint cloud to destroy the excess of carbonate. Tests were then made as before to determine how much one-thirtieth strength acetic acid was necessary to give maximum precipitation. This time only one-tenth of the estimated amount was used. The precipitate thus obtained formed the third fraction. The fourth fraction was obtained from this solution using the same plan as used in getting fraction number two except that one-tenth the calculated amount of dilute acetic acid solution was used the same as in fraction number three.

The small amounts of earths then remaining in solution formed the last two fractions. The carbonate solution in which they were dissolved was destroyed as before with nitric acid and the earths precipitated as hydroxides. The hydroxides were put into solution in ammonium carbonate and the fifth fraction extracted the same as the third. The earths remaining in solution then were taken as the sixth fraction. This was supposed to contain the most of the ytterbium, as the low atomic weight metals are supposed to precipitate first.

This series of fractions just described was known as Series 1.. Three other series of fractionations were run upon different fractions of the first series in order to get out all the ytterbium possible. The second series consisted of six fractions. The material used for this series of fractionations was obtained by putting together the largest part of the earths obtained in fractions 1 and 2 of series 1. Only a small amount of each fraction was saved as a sample and for atomic weight determinations. Series 3 consisted of 4 fractions and was made from a combination of the fifth fraction of the first series and the sixth fraction of the second series. Series 4 consisted of six fractions and was made from a combination of the third and fourth fractions of the first series and the fourth and fifth fractions of the second series.

## Atomic Weight.

The sulphate method was used in determining the atomic weight. The particular modification of this method that was used was the dissolving of the oxides in dilute hydrochloric acid and converting to sulphates by the addition of dilute sulphuric acid. The liquid was evaporated as far as possible on the water bath. Then the excess of sulphuric acid was driven off by heating the platinum crucible and contents in an asbestos nest in a large iron crucible.

Series 1—Fractionation

| Fraction | Wt. Gm. | Color of Oxide | At. Wt. |
|---|---|---|---|
| 1 | 550 | strong buff | 100.5 |
| 2 | 135 | buff | 100.2 |
| 3 | 85 | mild buff | 109.8 |
| 4 | 20 | nearly white, rose tint | 138.0 |
| 5 | 3.28 oxide | white, slight rose tint | 153.0 |
| 6 | 3.65 oxide | white | 173.5 |

The buff color is due to Terbium content. Its oxide is deep brown, but in small quantities gives buff.

## Series 2—Fractionation

Made from a combination of 1st and 2nd fractions of Series 1.

| Fraction | Wt. Gm. | Color of Oxide | At. Wt |
|---|---|---|---|
| 1 | 300 | very strong buff | 99.1 |
| 2 | 105 | strong buff | 101.7 |
| 3 | 90 | buff | 104.1 |
| 4 | 35 | slight buff | 113.9 |
| 5 | 8 | white, rose tint | 114.6 |
| 6 | 3.42 | white, slight rose | 146.7 |

## Series 3—Fractionation

Made from a combination of 5th fraction of 1st series and 6th fraction of 2nd series.

| Fraction | Wt. Gm. | Color of Oxide. | At. Wt. |
|---|---|---|---|
| 1 | 2 oxide | white, slight rose | 130.1 |
| 2 | 1.5 oxide | white, slight rose | 142.3 |
| 3 | 1.5 oxide | white, slight rose | 154.6 |
| 4 | 1.6 oxide | white | 163.2 |

## Series 4—Fractionation

Made from a combination of fractions 3 and 4 of the first series, and fractions 5 and 6 of the second series.

| Fraction | Wt. Gm. | Color of Oxide |
|---|---|---|
| 1 | 60 | Buff |
| 2 | 50 | Buff |
| 3 | 25 | Light Buff |
| 4 | 10 | Light Buff |
| 5 | 1.5 | Very light buff |
| 6 | 1.0 | White, slight rose |

The sixth fraction in this series gave an atomic weight of 146.

The last fraction in each series was examined with the spark spectrum. Each fraction examined showed the presence of ytterbium. As would be expected, the last fraction of the first series gave the strongest test, showing nearly pure ytterbium.

## Conclusion.

The research has shown that the method employed of fractioning yttrium group earths with dilute acetic acid in ammonium carbonate solution is a very satisfactory method. The last fraction of the first series gave an atomic weight of 173.5. When these experiments were finished this value was thought to be too high for pure ytterbium, but later atomic weight determinations show the correct atomic weight of ytterbium to be 173.5, which is exactly the atomic weight secured for this fraction which is supposed to be the fraction containing the purest ytterbium. In the past, thousands of fractionations have been made in order to separate out a single rare earth element. By the process presented here, very pure ytterbium was evidently prepared from Gadolinite in six fractionations.