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**STAPLER**

**Observations on the Rare Earths**

**Chemical Engineering**

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**OBSERVATIONS ON THE RARE EARTHS**

BY

**WILLIAM W. STAPLER**

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**THESIS**

FOR THE

**DEGREE OF BACHELOR OF SCIENCE**

IN

**CHEMICAL ENGINEERING**

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May 31, 1915

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

WILLIAM W STAPLER

ENTITLED OBSERVATIONS ON THE RARE EARTHS

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemical Engineering

*Carence V. Balke*

Instructor in Charge

APPROVED:

*W. A. King*

HEAD OF DEPARTMENT OF CHEMISTRY





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## OBSERVATIONS ON THE RARE EARTHS

The work outlined below consisted of the extraction of the rare earths from 100 kilograms of Gadolinite, and the preparation and analysis of several double selenates of samarium and neodymium.

### EXTRACTION OF THE RARE EARTHS FROM GADOLINITE

HISTORICAL. In 1794 Gadolin detected rare earths in a mineral afterwards called Gadolinite which had been found six years previously by Arrhenius near the town of Ytterby in Sweden.

This mineral is a basic orthosilicate of beryllium, iron and the yttrium metals of the formula  $\text{FeBe}_2\text{Y}_2\text{Si}_2\text{O}_{10}$ . The following analysis gives an idea of the general composition of Gadolinite:-

$\text{SiO}_2$	----	23.88
$\text{ThO}_2$	----	.41
$\text{Y}_2\text{O}_3$	----	45.30
$\text{Ce}_2\text{O}_3$	----	3.84
$\text{La}_2\text{O}_3$	)----	2.57
$\text{Di}_2\text{O}_3$	)	
$\text{FeO}$	----	12.89
$\text{Fe}_2\text{O}_3$	----	.60
$\text{BeO}$	----	9.91
$\text{CaO}$	)----	.54
$\text{MgO}$	)	
$\text{Na}_2\text{O}$	----	.15
$\text{H}_2\text{O}$	----	.57

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100.66



However, the composition varies greatly, for instance, the proportion of yttrium group oxides may vary from 22% to 46% while the cerium group oxides may run from zero to 51%.

While the extraction of the rare earths from 100 kilograms of this mineral was not completed, the mineral was worked up to a point where it can be successfully completed in the near future. After first being crushed to egg size it was reduced to the size of glass beads with the aid of a chip-monk mill and was then further reduced by running through a disc mill. Some trouble was experienced in getting the mineral reduced fine enough by this mill, as with the long continued grinding the plates were worn away quickly. After passing the mineral through this mill several times until it was almost in a powder form, it was placed in ball mills and allowed to run for four or five days. From the ball mills the Gadolinite was put through a "100 mesh" sieve, and it was then ready for decomposition. As soon as a quantity had passed through the above grinding process it was digested with concentrated hydrochloric acid in large evaporating dishes. Ten of these dishes were in use. Approximately two kilograms of mineral with about eight liters of acid were treated in each dish at one time. The digesting was continued until the mineral had decomposed, and the material was then placed in decanting jars and allowed to settle. The solution was too viscous, in most cases, for rapid filtration and hence water was added, after which it was decanted and filtered into a set of large jars. Twelve of these were kept running continually. The residue, which in some cases seemed to contain some undecomposed mineral, was placed again



in the evaporating dishes with more acid and perhaps a little fresh mineral. On the other hand, some of the solution was so strongly acid that it was placed again in the dishes with more of the mineral. This grinding, digesting, and filtering, was going on at the same time for about four months.

The filtrate, consisting of chlorides of practically everything in the mineral except silicon, was placed in carboys and the acid almost neutralized with ammonium hydroxide. Then, in order to isolate the rare earths, about 60 kilograms of commercial oxalic acid were dissolved and the solution filtered to remove the large quantities of packing straw, dirt, etc. This was added while hot to the nearly neutral chlorides as soon as a carboy of solution became ready. The oxalates of yttrium and cerium earths, with thorium, magnesium and calcium, were thus precipitated, leaving in solution the iron and beryllium. This solution was decanted, and together with the first washing, was stored in carboys for the beryllium contained therein. The oxalates were washed until free from chlorides, which necessitated about ten washings. These oxalates settled quickly which made the washing by means of a large syphon, comparatively rapid. Trouble was experienced with several carboys due to a quantity of iron which had collected on the bottom of the carboys. These were emptied of their contents and the lower portion containing the iron was digested with hydrochloric acid, and was then ready to be placed with the chlorides ready for the oxalate precipitation. As iron is just as easy to remove later on as at this point, a small amount in several carboys was not taken out.



After washing these oxalates free from chlorides they were dried in an oven and were then converted into sulphates by mixing with concentrated sulphuric acid until a slightly damp, crumbly mass was formed. This was placed in seven and nine inch evaporating dishes on tripods which were surrounded and covered with asbestos. Here the material was heated until no further sulphuric acid could be driven off, which took from twelve to fifteen hours for each dish.

At this point other work was taken up. As the percentage of cerium group earths was small, it was intended to convert these sulphates directly to bromates with barium bromate, instead of first separating out the members of the cerium group as double alkali sulphates. About twelve kilograms of sulphates were prepared and over sixty kilograms of washed oxalates, while there was still two large decanting jars of decomposed mineral which had not been leached, and which should yield at least twenty-five more kilograms of oxalates.

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#### PREPARATION AND ANALYSIS OF DOUBLE SELENATES

The second part of the work was of an entirely different nature, and consisted in the preparation and analysis of double selenates. The first salt made was the double selenate of rubidium and samarium. Supposing that the salt would contain equi-molecular proportions, the volume of selenic acid was calculated to unite with six grams of samarium oxide, and an equi-molecular proportion of rubidium selenate was added to this. No salt came out. An attempt





was then made to concentrate the solution by placing it over a small lamp which raised the temperature to about 40°C and by blowing air through the solution. The salt was very soluble and nothing came out after about four hours. After this time a white substance began to appear. It was filtered off and the filtrate placed in a vacuum dessicator and slowly evaporated. It was left there for two days and then plate-like crystals of a yellow color characteristic of samarium compounds began to form. By the end of ten days a sufficient quantity of these crystals had separated for analytical determination. These were washed, centrifuged, and air dried.

After making up solutions of samarium and potassium selenate, the double selenate was prepared in the same manner as above.

Next an attempt was made to prepare the complex ethyl amine neodymium double selenate. Solutions of ethyl amine selenate and neodymium selenate were made up. After mixing the two solutions and allowing the mixture to remain about ten days in a vacuum dessicator, pink feathery crystals appeared. Some of these were carefully washed and centrifuged until free from the mother liquor, and then decomposed with sodium and tests made for nitrogen. As no trace of nitrogen was found, it was concluded that the salt was simply neodymium selenate, and that it was not possible to form the double salt. Neodymium selenate has never been prepared before, however, and in this case the salt formed by slow concentration was quite different from the neodymium selenate which came out on heating the solution.



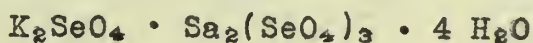
Analyses were made of three double salts. The same method was followed in all cases. The selenium was determined first, then the earth contained in the salt, and lastly the metal. As the selenium was in the form of a selenate it had to be reduced first to a selenite. This was done by means of concentrated hydrochloric acid on the dry salt, which was found to be much better than long continued boiling with dilute acid. The selenium was then brought down as elementary selenium by passing in sulphur dioxide under slight pressure. It first appeared as a light brick red precipitate and then turned darker gradually. Then the solution was boiled to drive off the sulphur dioxide. The selenium turned still darker red and finally caked together in most instances as a grayish black mass. After filtering through Gooch crucibles and washing with water and then with alcohol, the selenium was dried at from 105° to 110°C in an electric oven and weighed. The filtrate was evaporated to dryness on a water bath in order to get rid of the excess of hydrochloric acid. The residue was then taken up with water and a little acid, but a precipitate formed, a small quantity of which would not dissolve even in concentrated hydrochloric acid. This precipitate came down in all the determinations, but as it was very small in quantity it was filtered off and discarded. It resembled silica but this was not determined. Ammonia was added to precipitate the earth as hydroxide, which was dried and ignited to oxide. Some difficulty was encountered in trying to get the weight of the oxide constant, as different weighings showed that it kept increasing from one to five millograms at each weighing. It was at last obtained constant in the various analyses.



The filtrate which contained alkali metal in ammoniacal solution was evaporated to dryness on the water bath and then taken up with a little sulphuric acid and then evaporated to dryness in a muffle at a gentle heat while the sulphuric acid continued to come off. In the case of the potassium samarium double selenate, potassium thiosulphate, as well as potassium sulphate, was probably present at this time, and a little solid ammonium carbonate was added. In this manner the excess of sulphuric acid was converted into ammonium sulphate which could be volatilized at a much lower temperature than that necessary to convert the thiosulphate to sulphate, which would probably have involved a loss of some of the potassium.

The results of the analyses are as follows:-

POTASSIUM SAMARIUM DOUBLE SELENATE



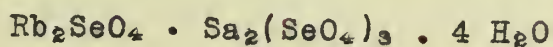
<u>Found</u>		<u>Theory</u>
7.46%	----- K -----	7.63
32.58	----- Sa -----	29.36
54.32	----- SeO <sub>4</sub> -----	55.97
5.64	----- H <sub>2</sub> O -----	7.04

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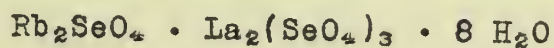
## RUBIDIUM SAMARIUM DOUBLE SELENATE



<u>Found</u>		<u>Theory</u>
16.44%	----- Rb -----	15.33
28.54	----- Sa -----	26.90
47.60	----- SeO <sub>4</sub> -----	51.30
7.42	----- H <sub>2</sub> O -----	6.45

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## RUBIDIUM LANTHANUM DOUBLE SELENATE



<u>Found</u>		<u>Theory</u>
14.86%	----- Rb -----	14.68
24.42	----- La -----	23.86
48.47	----- SeO <sub>4</sub> -----	49.09
12.25	----- H <sub>2</sub> O -----	12.36

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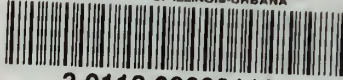
I wish to express my thanks to Professor C.W.Balke for his assistance and guidance in this work.







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