SEPARATION OF IRON, ALUMINUM, CALCIUM,, AND MAGNESIUM FROM PHOSPHORIC ACID

by

THOMAS KING COX

A THESIS SUBMITTED FOR
THE DEGREE OF BACHELOR OF SCIENCE

CHEMICAL ENGINEERING COURSE

University of Tennessee

1924

CONTENTS

Introduction

This is a study of the quantative separations of iron, aluminum, calcium, and magnesium, from phosphoric acid. Since all these elements are contained in phosphate rock, it was chosen as the material on which this work would be carried out. In the case of most minerals, a sample is dissolved in acid, and silica filtered off, the iron and aluminum precipitated as hydroxides with ammonium hydroxide, and filtered off, leaving a filtrate containing calcium and magnesium. The calcium is precipitated from an ammonical solution as calcium oxalate, filtered off, and the magnesium precipitated from the filtrate as ammonium magnesium phosphate.

When phosphoric acid is present, the above scheme will not work. When ammonium is added to precipitate the iron and aluminum the phosphoric acid also goes down taking with it some of the calcium, and magnesium. This being the case iron and aluminum must be separated from the solution in some way that will not cause the precipitation of the phosphoric acid. Also there must be some way of separating the phosphoric acid from the solution that will not cause any of the calcium, and magnesium to be precipitated.

There is a report on the analysis of phosphate rock in the Journal of Industrial, and Engineering Chemistry, made by the Committee on Research and Analytical Methods. This report consists in the methods of the selection of samples, and the determination of the phosphoric acid content of the rock.

There is also given a method for the determination of moisture, iron, and aluminum. These methods are very accurate when carried out with great care, but are too long and complicated to be used to an advantage in a commercial laboratory, where many samples must be run in the course of a day. There are no method given for the determination of calcium, or magnesium in the presence of phosphoric acid.

In many books on analytical methods there are schemes given for the separation of phosphoric acid from these elements, but these separations are for the purpose of determining the amount of phosphoric acid, and not the other elements. As in the case of the precipitation of phosphoric acid, as phosphomolybdate, there has been made a quantative separation of the phosphoric acid but to make this separation there was added an excess of ammomium molybdate, and the separation of iron, aluminum, calcium, and magnesium from the molybdate filtrate is as large a problem as the separation from the phosphoric acid.

This work was started for the purpose of making a study of the separation of iron, aluminum, calcium, and magnesium in the presence of phosphoric acid and to test out some of the proposed methods for separation of these elements; and if possible to determine some practical method of analysis of a substance containing these elements, that will be rapid, and have a fair degree of accuracy.

A sample of phosphate rock which was gotten from the Bureau of Standards, was used for this work. It was ready to be put in solution by the treatment with acid.

The phosphoric acid content was the only percentage known, so a complete analysis was made first, and the results from it were considered as correct. Then other methods of separation for the different elements were carried out, and results compared with the results from the complete analysis.

The complete analysis and all the comparative tests were carried out using the apparatus and equipment found in any well equipped chemical laboratory. No special apparatus was required. The following are the detailed methods of procedure by which the analysis of the phosphate rock was made.

Analysis of Phosphate Rock

Determination of moisture.

The percent of moisture in the phosphate rock was determined by weighing out exactly 20 grams of the finely powdered rock in a weighed 4 inch platinum dish, this was placed in an oven in which the temperature was kept between 100 and 110 degrees C. After it had been in the oven for two hours it was removed, allowed to cool in a desiccator, and weighed. It was then placed back in the oven, this time it was kept in the oven an hour then cooled and weighed. The heating and weighting was repeated until a constant weight was obtained.

This weight was subtracted from the weight of the sample plus the weight of the platinum dish, leaving the weight of the moisture that had been driven off. This weight of moisture was then divided by the weight of the original sample, giving the percent of moisture in the phosphate rock.

The contents of the platinum dish was transfered to an 8 inch casserole, and the dish washed out with distilled water. 75cc. of concentrated hydrochloric was added and the casserole covered with a watch glass, and placed on a hot plate, care being taken not to let the reaction take place too rapidly. The speed of the reaction was regulated by the amount of heat that was applied. While the reaction was taking place the mixture was stirred at intervals. When all the reaction had about ceased, 50 cc. of nitric acid was added, and again the speed of the reaction was regulated by the heat that was applied. As soon as reaction ceased the solution was placed over the hot part of the hot plate and carried to dryness, then baked for 30 minutes. It was taken up 75 cc. of hydrochloric acid, and when all soluble matter had been dissolved, the solution was carried to dryness again, and baked for 30 minutes to dehydrate the silica. This time it was taken up with 75 cc. of hydrochloric acid, and when it was all dissolved except the insoluble residue or silica, 400 cc. of water was added, and the solution brought to a boil. After boiling for about 10 minutes, it was filtered while hot, and washed with hot water. The insoluble residue on the filter was placed back in the casserole and the above treatment repeated.

The filtrate was evaporated to dryness, and taken up with hydrochloric acid, again carried to dryness, and baked to dehydrate the remaining silica. After baking for about 30 minutes the residue was taken up with 50 cc. of hydrochloric acid and diluted to about 300 cc., filtered and washed with hot water until free from the chlorides.

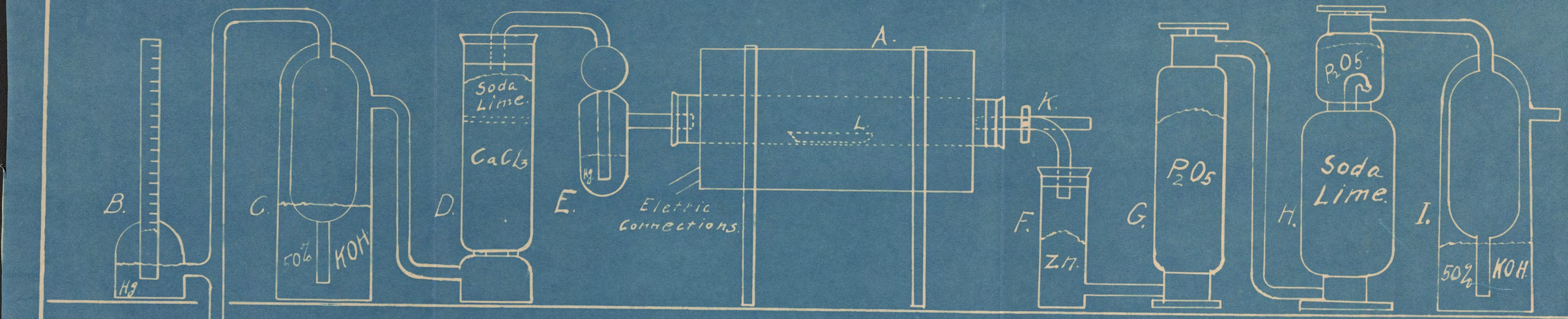

FIGURE No. 1. COMBUSTION APPARATUS.

A-MULTIPLE UNITE ELECTRIC COMBUSTION FURNACE.
B-MERCURY PRESSURE GAUGE C and I-WASHING BOTTLES.
D-CALCIUM CHLORIDE JAR. E-MERCURY VALVE. F-ZINC JAR.
H-FLEMING ABSORBTION TUBE. G-PHOSPHORIC ANHYDRIDE JAR.
J-SILICA TUBE 30" K STOP COCK. L-CLAY BOAT for SAMLPLE.

T. K. Cox.

This filtrate was added to the filtrate from the insoluble residue, and diluted up to one liter. One cc. of this solution contains 0.2 grams of the phosphate rock, and will be refered to as solution A.

Loss on Ignition.

This determination was made by placing a gram sample in a weighed crucible and ignited over a blast lamp for 15 minutes, then placed in a desiccator and allowed to cool to room temperature. While being ignited all the carbon dioxide, moisture, and organic matter present in the rock are driven off. After it is cool it will take up moisture and carbon dioxide from the air. For this reason the approximate of weights was placed on the balance before the crucible was then placed back in the desiccator, and then the reading of the weight on the balance was taken. This process was repeated until a constant weight was subtracted from weight of the sample leaving the weight of the carbon dioxide, moisture and organic matter that had been driven off, or what is commonly termed loss on ignition. This weight divided by the weight of the sample gave the percent of loss on ignition.

Determination of Carbon Dioxide

This was made with Flrming's Apparatus for determinating carbon dioxide by combustion. Apparatus shown in Fig. 1. After the furnace had been heated up to 1000 degrees C., the air was swept out and the train purified by passing oxygen through for about 15 minutes at the rate of 300 cc. per minute. As soon as the oxygen was cut off the cock K. from J. to F. was closed, and thenostoppers in G. were closed.

Then the stoppers in the absorbing tube were closed, bottom first, the absorbing tube was then removed from the train, and weighed. It was placed back in the train, and oxygen passed through the entire train for a few minutes. Then the cock K. was closed and the boat L. containing about a gram of the phosphate rock was pushed up in the silica tube J. until it was in the hottest part of the furnace, the stopper placed back in J. the cock K. opened, so that the oxygen could pass on out through the train. The carbon dioxide was driven off from the sample in the boat, and carried by the oxygen to absorbing tube where it was absorbed. After 15 minutes the oxygen was cut, the cock K. closed, and the stoppers to G. and H. closed. H. was then removed from the train, and weighed, the increase in weight was the weight of the carbon dioxide in sample, this divided by the weight of the sample gave the percent of the carbon dioxide in the phosphate rock.

Determination of Silica

Two grams of the phosphate rock were placed in a No. 3. beaker and 25 cc. hydrochloric acid (specific gravity 1.20) added, a watch glass placed over the beaker and set on a hot plate. When all reaction had ceased 10 cc. of nitric acid was added, when this reaction ceased the solution was carried to dryness, and the residue baked for 30 minutes to dehydrate the silica. The soluble part of the residue was taken up with 25 cc. of hydrochloric acid, and again carried to dryness and baked. This time it was taken up with 25 cc. with distilled water, filtered through an ashless filter paper, and washed free of chlorides with hot water. The insoluble residue on the filter paper was dryed, ignited and weighed as SiO_2. The weight of the

SiO2 divided by the weight of the sample gave the percent of the SiO2 in the phosphate rock.

Determination of Sulphur

The determination of sulphur was made from the filtrate from the silica determination, which was a hydrochloric acid solution. This solution was heated to nearly boiling 25 cc. of barium chloride solution was added slowly with constant stirrings of the solution. The solution was kept at a temperature that was a little below boiling for 3 hours. It was then filtered through a double filter of ashless filter papers, and washed several times with hot water. The filter and the residue were then dryed in the oven, then ignited over the bunsen burner, and weighed as BaSO4. The weight of the BaSO4 was multiplied by .3430 to get the of SO3, which was divided by the weight of the sample to get the percent of SO3.

CaSO4-BaCl2--BaSO4-CaCl2.

Determination of Ferrio Oxide

The sample for this determination was 100 cc. of solution A. when was measured with a pipette. The samples was placed in a No. 3 beaker 10 cc. of nitric acid added and the solution boiled. When the solution was cool 20 cc. of Sulphuric acid was added the solution heated nearly to boiling. The solution was reduced from the ferric conditions to ferrous, by passing it through a Jones reducor. After the reduction was complete the solution was titrated with a standard solution of Potassium Permanganate. This standard solution of Potassium Permanganate had an iron value of .00868 gram per

cc. The calculations were made with the following formula.

$$\frac{\text{No. cc. of } KMnO_4 \times .00868 \times 100}{\text{Weight of the sample.}} \text{ --\% of Fe.}$$

% of Fe. x 1.4298 -- Fe 203.

The reaction which occur in the iron determination.

Fe_2O_3-HCL--$2FeCl_3$-$3H_2O$.
$2FeCl_3$-$3H_2S$-4--$Fe_2(SO_4)_3$-6HCL.
ZnH_2SO_4--ZnS-4-H_2.
$Fe(SO_4)_3$-H_2--$2FeSO_4$-$2H_2SO_4$.
$10FeSO_4$-$2KMnO_4$-$8H_2SO_4$--$5Fe_2(SO_4)_3$-K_2SO_4-$2MnSO_4$-$8H_2O$

Determination of Aluminum Oxide

This was made by separating the aluminum from the other elements as aluminum phosphate. The determination was carried out as follows. 100 cc. of solution A. was placed in a No. 3 beaker, and diluted with distilled water to 300 cc., ammonium hydroxide was added until the solution was nearly neutral but did not show any precipitate. 3.3 cc. of hydrochloric acid was added to the nearly neutral solution, then a solution of two grams of sodium phosphate was added. To this solution 10 grams of sodium thiosulhate was added followed with 15 cc. of (1-1) acetic acid, then it was heated to boiling and let boil for exactly 15 minutes. The solution was filtered through an ashless filter paper while hot, to increase the speed of the filtering suction was applied. After all the precipitate had been transfered to the filter it was washed ten to twelve times with hot water. The residue on the filter was then dryed, and ignited in a porcelain crucible, just enough heat being applied to burn off the carbon. When all the carbon had been burnedd off and the residue cooled it

was weighed as AlPO4. This weight multiplied by .4185 gave the weight of the Al2O3. This was divided by the weight of the samples to get the percent of Al2O3 in the phosphate rock.

Determination of Phosphoric Acid

25 cc. of solution A. was placed in a 700 cc. flask and diluted to 75 cc. with distilled water. Strong ammonia was added and solution shaken vigorously, the addition of ammonia and shaking continued until the solution smelled of the reagent. Then just enough strong nitric acid was added to dissolve the precipitate which had been formed by the addition of the ammonia, the flask was shaken while the nitric acid was being added. Then 100 cc. of ammonia molybdate was added, a cork place in the flask and the flask shaken for 5 minutes. Then the flask was placed in a warm place (near a blast lamp) for 30 minutes so that the yellow precipitate of phosphomolybdate could settle. After the precipitate had settled a small amount of ammonium molybdate was added to determine if the precipitation was complete. The yellow precipitate was separated from the solution by filtering, and was washed with a 1 % solution of nitric acid and followed by a 1 % solution ammonium nitrate.

The precipitate of phosphomolybdate was dissolved off the filter by the addition of 20 cc. of ammonium hydroxide, the solution being caught in the same flask in which the precipitate had been made. After all the precipitate had been dissolved and the paper washed with water, the solution

was cooled, and the excess of ammonia neutralized with hydrochloric acid, the hydrochloric acid was added until the yellow precipitate which formed by the neutralization was difficultly dissolved. To the cold solution 20 cc. of cold magnesia mixture was added drop by drop with constant stirring. When the precipitate began to form the stirring was discontinued, and the precipitate allowed to settle for about ten minutes. Then 60 cc. ammonium hydroxide was added and the solution well stirred, the precipitate settle over night, and filtered through an ashless filter paper. The precipitate was washed with dilute (1-4) ammonium hydroxide. The precipitate was then dryed, ignited over bunsen burner, heat was applied very gently and gradually increased until the residue became a light gray color. It was then weighed as $Mg_2P_2O_7$.

The weight of $Mg_2P_2O_7$ was multiplied by .6779 to get the weight of P_2O_5, this was divided by the weight of sample taken to get the percent of P_2O_5 in phosphate rock.

$H_3PO_4 - 12(NH)_2MoO_2 - 21\ HNO_3 -- (NH_4)_3PO_4.12MoO_4 - 21\ (NH_4)NO_3 - 12H_2O.$

Determination of Calcium.

Before the calcium and magnesium can be determined, the phospheric acid has to be removed. In this analysis it was removed by adding enough iron salts to combine with the phosphoric acid that is not already combined with the iron and aluminum that is in the rock. The iron and aluminum phosphate was then precipitated with ammonium acertate in a slightly acid

solution.

The process was carried out as follows. A sample of 25 cc. of solution was placed in No. 4. beaker diluted to about 100 cc. and 150 cc. of 15 % solution of ferric chloride add. Then ammonium hydroxide was added until the solution was nearly neutral, but not neutral, (slightly acid). A slight excess of ammonium acetate was added and the solution heated up just to boiling, then removed from the heat, and the precipitate allowed to settle. It was filtered, using a large funnel and filter paper, it was washed several times with boiling hot water. The filtrate was again treated with ammonium acetate to remove what aluminum and phosphrous, that might be left in it. The filtrate this time was caught in a No. 4 beaker and marked filtrate No. 1.

The two precipitates were dissolved with dilute hydrochloric acid and the above precipitation repeated. This filtrate was treated with a second portion of ammonium acetate, boiled and filtered. This filtrate was added to filtrate No. 1 and evaporated down to about 300 cc. This solution was then free from iron, aluminum, and phosphrous, and was ready for the determination of calcium and magnesium.

This 300 cc. solution was made alkaline with ammonium hydroxide and stirred well, an excess of ammonium oxalate was added and then heated to boiling. The precipitate was allowed to settle; but the solution was kept hot. While the solution was still hot the supernatant liquid was poured through a filter, the precipitate washed with hot water by de-

cantation several times, then transfered to the filter-paper, and washed. The precipitate was dissolved off the filter paper with dilute hydrochloric acid, after all the precipitate had been dissolved off the paper it was wrinched off with dilute ammonium hydroxide.

The Filtrate was diluted up to 150 cc. and made alkaline with ammonium hydroxide, allowed to settle. It was then filtered through the same filter as before, washed until filtrate gave no trace of chloride. The filter paper was removed from the funnel and placed in 300 cc. of hot 1-50 dilute H_2SO_4. When all the calcium had been dissolved, the solution was titrated with a standard solution of potassium permanganate, until the solution turned slightly pink. The calcium standard for the solution of potassium permanganate was .00434 grams of calcium per cc. The percent of calcium was gotten by multiplying the number of cc. of potassium permanganate used by .00434, and dividing by the weight of the sample taken.

Determination of Magnesium

The filtrates from the calcium precipitates were added together, made acid with HCL, and evaporated down to about 400 cc. This solution was made alkaline with ammonium hydroxide, and 25 cc. of sodium phosphate solution was added, then ammonium hydroxide equal to 1/10 of the original volume was added. The precipitate was allowed to settle over night, then filtered, washed until free of chloride, then dryed, and ignited over bunsen burner, the heat was increased gradually until the residue became a dull red. When the residue had cooled to room temperature it was weighted as $Mg_2P_2O_7$.

This weight multiplied by the factor .3621, and divided by the weight of the sample gave the percent of magnesium oxide in the phosphate rock.

The following are the Aneroge Results of the analysis.

Empirical.		Rational.	
H_2O	.33%	H_2O	.33%
Loss on Ignition	2.28%	Loss on Ignition.	2.28%
SiO_3	27.77%	SiO_2	27.77%
Al_2O_3	1.55%	Al_2O_3	1.55%
Fe_2O_3	2.90%	Fe_2O_3	2.90%
P_2O_5	25.50%	$Ca_3P_2O_8$	55.68%
CaO	34.62%	$CaSO_4$	1.20%
MgO	1.13%	$CaCo_3$	7.04%
CO_2	3.04%	MgO	1.13%
SO_3	.71%		
Total.	99.83%	Total	99.88%

-Comparison of Separations-

The total percent of the above analysis checks with in .17 of 100%, leaving an average error of .017 for each determination. This being a very small error the above analysis was considered as a correct basis of comparison for testing other methods of separations.

After making a study of the different methods that are given for the determination of iron and determination of aluminum in the presence of phosphoric acid, it was found that the method used in the above analysis to be about the shortest

and simplest that would give accurate results.

The problem was then to find some easy to make a complete separation of the phosphoric acid from the calcium and magnesium, leaving them in such a condition that their percent could be determined. The separation by basic acetate method, which was used in the above analysis, is very accurate, but is long, and tedious, requiring several precipitations to get a good separation. These precipitates are very large and voluminous, and hard to wash clean. This makes it a very impractical method to be used in a commercial laboratory. Several methods were tried, but none were found that would meet the requirments and still give accurate results.

Precipitation of phosphoric acid as a stannic phosphate.

This was carried out by the method given in Fresenous (134, page 277.) 25 cc. of solution A. was carried to dryness, taken up with 25 cc. of nitric acid, diluted to about 100 cc. with water and the chlorides present precipitated with silver nitrate. To this solution free from chlorides, tin foil was added until there was eight times as much tin present as there was phosphorous. This was heated for 5 or 6 hours and the precipitate was allowed to settle. The precipitate was washed several times by decantation with hot water, finally it was transfered to the filter and washed more. The precipitate consisted of metarstannic and stannic phosphates, together with a little ferric and aluminum phosphates. This precipitate was treated with an excess on ammonium sulfide; water containing some ammonium sulfide. The precipitate consists of ferrous sulfide and aluminum hydroxide.

It was intended that this precipitate should be dissolved with nitric acid, and the solution added to the filtrate from the stannic precipitate, and that this solution be used for the determination of iron, aluminum, calcium, and magnesium. At this point the method was abandoned because the precipitates that had to be filtered were so large and hard to filter, and wash that it required too much time to be used for practical purposes.

Precipitation of phosphrous with ammonium molybdate.

A 25 cc. of solution A. was taken, the phosphorous precipitated with ammonium molybdate in the same manner as in the complete analysis. Then attempt was made to precipitate the excess of molybdate from the filtrate by passing in hydrogen sulfide, but this proved unsatisfactory due to the nitric acid which was in the solution. The hydrogen sulfide produces a precipitate but it was dissolved by the HNO3 nearly as fast as it was formed.

Precipitation of calcium as calcium oxalate.

By this method the calcium was precipitated as calcium oxalate while the precipitation of aluminum, iron, and phosphoric acid was supressed by an excess of citric acid. This was carried out by method given on Scott, (Vol. 1. page 106). A sample of 25 cc. of solution A. was taken, 75 cc. of ferric chloride solution added and oxidized by boiling with nitric acid as usual. The solution then diluted to about 300 cc. and cooled to room temperature. Ammonium hydroxide was added to the cool solution until a slight precipitate formed, this was dissolved by the addition of citric acid, more ammon-

ium hydroxide added until precipitate formed and this was again dissolved with citric acid. The addition of ammonium hydroxideand citric acid was continued until the addition of ammonium hydroxide cause no precipitate to from, then 15 cc. in excess of the citric acid was added. The solution was then heated to boiling, the calcium precipitated with ammonium oxalate in the usual way, filtered, washing it in hot dilute solution of sulphuric acid and the solution titrated with a standard solution of potassium permanganate.

There were two determinations made by this method, the results were low, and not consistent. The results were 29. 93% and 29.25% of CaO.

Precipitation of calcium as calcium sulfate

This separation based on the fact that CaSO4 is insoluble in an alchol solution. 25 cc. of solution A. was placed in a No. 3. beaker, and carried to dryness, taken in with 25 cc. of hydrochloric acid, and the solution allowed to cool to room temperature. 20 cc. of sulphuric acid (1-1) was added to the cool solution, followed by the addition of 50 cc. of alcohol. The precipitate was allowed to settle for two hours, then filtered through a weighed gooch crucible, and washed with alcohol. After the residue in the Gooch crucible was dry, it was ignited over a bunsen burner to a red heat, cooled in a desiccator and weighed as CaSO4. There were three determinations made by this method giving the following results; 30.41%, 32.99%, and 32.14% of CaO.

APPROVAL

The foregoing thesis is hereby approved as a creditable study of an engineering subject, carried out and presented in a manner sufficiently satisfactory to warrant its acceptance as a prerequisite to the degree for which it has been submitted. It is to be understood that by this approval the undersigned dose not necessarily endorse or approve any statement made, opinions expressed, or conclusions drawn therein, but approves the thesis only for the purpose for which it is submitted.

Name Chas. O. Hill

Title Prof. of Chemistry