ROCK PHOSPHATE FUSIONS WITH AMMONIUM SALTS

By

Neville Campbell

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HISTORICAL INTRODUCTION

Early History of Rock Phosphate

Apatite was at first confused with other minerals; however, in 1786, A. G. Werner recognized it as a distinct mineral species. The mineral was analyzed by M. H. Klaproth and L. N. Vauquelin and found to contain lime and phosphoric acid. (1).

The results of this analysis immediately established apatite as one of the most important mineral species, for the importance of phosphate had long been recognized. Numerous other analyses, of apatite, were made; and it was found that the composition, although similar in the main constituents, varied according to the location of the deposit.

The principal constituent of apatite was found in most cases to be $Ca_3(PO_4)_2$. This, of course was combined with other compounds, such as those of iron and aluminum. (1) These analyses showed that, although phosphate was present in the rock, it was not readily available to plants in its existing form.

Early Investigations

As would be expected, the first experimental work and investigations carried out with apatite were attempts to determine its properties. The rock was thoroughly analyzed and many of its chemical and physical properties were determined.

The first fusion work of any nature that was done with apatite was in 1854 when P. W. Forchhammer found apatite to be readily soluble in molten sodium chloride. (2) On cooling, the dissolved apatite separated out in long needles. P. A. Wagner made use of this discovery, that apatite was soluble in molten sodium chloride, to separate it from kimberlite. (3).

The melting point of apatite was found to be about 1300°C. ;however, it will dissolve in fused microcosmic salt to a clear glass which, on cooling, freezes to a white enamel. (4).

The first compound that was made from rock phosphate by fusion was prepared in 1886. A. Ditte prepared bromophosphate by fusing together sodium bromide and rock phosphate (1) according to the equation:

$$Ca_3(PO_4)_2 - CaBr_2 \xrightarrow{\text{Fused}} Ca_3(PO_4)_2CaBr_2$$

Fused borax was found to behave similarly to sodium chloride and W. Florence obtained crystals of sodium phosphate from such a fusion. (4). According to C. F. Plattner, fused sodium carbonate will dissolve and decompose apatite.

No report of these early investigations gives any indication of an attempt to produce a commercial fertilizer from rock phosphate, by fusion with other salts.

With the beginning of the twentieth century

the importance of rock phosphate for fertilizer manufacture became more widely recognized. Many methods of treatment of the rock by acid were studied and the patents came thick and fast. In 1907 a study was made of the decomposition of the rock by water (5) and a process for manufacture of $CaHPO_4$ by a method of treatment with H_2SO_4 (6) and precipitation from a water solution (6) was discovered and patented.

Later Work With Fusions

Many attempts to produce apatite synthetically by fusion methods had been attempted; however, it remained for P. A. Wagner to actually succeed. In 1909 Wagner made apatite by fusing ground rock and sodium chloride. (3).

The synthetic production of apatite now being understood, most of the study turned toward making the P_2O_5 of the rock phosphate available. Rock phosphate was calcined and the effect of calcining on the availability of the P_2O_5 (7) and solubility (8) was determined. These studies revealed that calcined rock phosphate was only slightly more soluble but that when the rock is fused the phosphate is much more readily available than in the natural occurring rock phosphate. (9).

In 1915, Mourels succeeded in making a phosphate compound from rock phosphate. By fusing

rock phosphate with an excess of chloride in a crucible, the tribasic phosphate was made to combine with the chloride to form chlorophosphate. (10) This work was followed up by Menminger who combined rock phosphate with SiO_2 by a calcining process at 1400-1500 C. (11).

Hillebrand and Lundell studied the losses of P_2O_5 from fusion of rock phosphate and found them to be very slight. (12) Volatilization of P_2O_5 started at about 270 C. however, even at very high temperatures the amount of P_2O_5 volatilized was almost negligible.

In 1921, Diekmann and Houdremont made some studies on the fusion of $Ca_3(PO_4)_2$. (13) They found that when heated to 400-500 C. a more insoluble basic phosphate was formed which was decomposed at higher temperatures into the normal salt. This intermediate salt was thought to be oxy-apatite, $3Ca_3P_2O_5CaOCa_3P_2O_5$.

Blumenberg, in 1926, prepared a mixture of ground rock phosphate and K_2SO_4 and heated it until the mass fused. The fused mass was then pulverized and treated with water and SO_2. This treatment resulted in producing potassium phosphate. (14) This same year Fishburne calcined rock phosphate with Na_2SO_4 and obtained a porous mass almost entirely P_2O_5 citrate soluble. (15).

A year later in 1927 Blumenberg revised

his process and heated ground rock phosphate with $(NH_4)_2SO_4$ in a closed retort to above 300 C. and formed ammonium phosphate and calcium sulphate. (16) The temperature employed by Blumenberg was too high for the production of dicalcium phosphate. According to Larson, (17) who studied the preparation of dicalcium phosphate and the effect of temperature on it, heating the salt for five hours at 108, 150, and 150-185 C. caused a loss equivalent to one molecule, two molecules, and three to four molecules of water respectively. (18) At slightly higher temperatures the salt was transformed into pyrophosphate completely. Thus, with the temperatures employed by Blumenberg, any dicalcium which might have been formed would have been converted into pyrophosphate.

Summary

The work of these early investigators has shown that rock phosphate is soluble in many fused salts and is decomposed by most of them. It has further been shown that rock phosphate can be made to combine with some salts by fusion.

Especially important is the work of Blumenberg who fused $(NH_4)_2SO_4$ with ground rock phosphate in a closed retort and produced ammonium phosphate. This salt, containing both phosphate and

nitrogen, has possibilities as a commercial fertilizer. In this fusion Blumenberg went to temperatures well above the decomposition point of dicalcium phosphate. Thus, should any dicalcium phosphate have been formed during the fusion it would have been decomposed by the high temperature. By the use of lower temperatures both dicalcium and ammonium phosphate might possibly be formed. Reactions with other ammonium salts might also be obtained by fusion processes.

OBJECT OF INVESTIGATION

The object of this work is to investigate the possibility of producing a good commercial fertilizer, substantially corresponding to $CaHPO_4$, from rock phosphate by means of fusing with ammonium salts.

The value of treating land with fertilizer has long been recognized and the manufacture of fertilizer is today one of our leading industries. One of the most important sources of raw materials used in the manufacture of fertilizer is rock phosphate. This rock occurs naturally in various spots through out the world; however, our main interest lies in those deposits found in Tennessee.

Rock phosphate in its natural form is of little value as a fertilizer but it is converted into useful forms by various treatments. The most important form produced is monocalcium phosphate of superphosphate.

Monocalcium phosphate, $CaH_4(PO_4)_2$ is made by the action of H_2SO_4 on phosphate rock. This reaction proceeds according to the equation:

$$Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4$$

A still better product is triple superphosphate, $3CaH_4(PO_4)_2$, which is made by the action of phosphoric acid on the rock phosphate. This reaction proceeds to the equation:

$$Ca_3(PO_4)_2 + 4H_3PO_4 = 3CaH_4(PO_4)_2$$

The triple superphosphate is a much more concentrated fertilizer than the superphosphate. In the case of the former, all the phosphate in the product is supplied from the rock phosphate. However the process yields a product that is not very rich in phosphates, that is likely to contain free acid, and that is water soluble. On the other hand the triple superphosphate also has some objections. It is water soluble and most of the phosphate in the superphosphate comes not from the rock phosphate but from the phosphoric acid, which must be made and is an expensive material.

A much better product to be desired, in some cases, than either of the two named above is dicalcium phosphate, $CaHPO_4$. Dicalcium phosphate is a neutral salt which is not water soluble but is available to plants since it is dissolved by soil solutions.

The methods of preparation of dicalcium phosphate that are in use today are precipitation methods. These methods, while yielding a pure, high grade product, are much too expensive for practical use as a commercial fertilizer.

Attempts have been made to prepare dicalcium phosphate by limiting the amount of phosphoric acid used in making superphosphate and obtain dicalcium phosphate thus:

$$Ca_3(PO_4)_2 + H_3PO_4 = 3CaHPO_4$$

This work, while still in the experimental stage, has been unsuccessful. Instead of going to dicalcium phosphate, as hoped, the process merely yields a partial conversion to the superphosphate.

In attempting to find other methods for production of a good cheap fertilizer, we turn to fusion methods. In this we are limited since dicalcium phosphate will decompose at a little over 200 C. in an atmosphere of steam. (20) This limits our field to those salts that will fuse below about 200 C. It is also necessary to limit the field still further. The product that is obtained must not contain substances that would be harmful. In choosing salts to fuse with the rock phosphate we must choose a salt, which if it reacts, will not form a compound that would be injurious to plants. A salt with a volatile anion seems to be the solution since on fusion the anion would be driven off and leave only the desirable constituents in the product.

For our purpose ammonium salts were chosen since they fill all the requirements we have assumed necessary for fusion with the rock. For this investigation we have chosen three ammonium salts, fusing below 200 C., that seem to be the most promising. The salts chosen were: $(NH_4)_2HPO_4$, $NH_4H_2PO_4$, and NH_4HSO_4.

These salts of ammonia fuse below the decomposition point of $CaHPO_4$, so that a reaction

might take place to give $CaHPO_4$ as one of the products. The possibility of such a reaction represented by the following equations has been investigated.

I. Monoammonium Phosphate- $NH_4H_2PO_4$

$$Ca_3(PO_4)_2 + NH_4H_2PO_4 = 3CaHPO_4 + NH_3$$

$$CaF + NH_4H_2PO_4 = CaHPO_4 + HF + NH_4F$$

These equations show the reaction that is hoped to be produced and take into account the calcium that is combined with the fluorine as well as that that is combined with the phosphate.

II. Diammonium Phosphate - $(NH_4)_2HPO_4$

$$Ca_3(PO_4)_2 + (NH_4)_2HPO_4 = 3CaHPO_4 + 2NH_3$$

This equation is similar to the one for the monoammonium salt except in this case two moles of ammonia are given off as compared with only one mole in the previous case. It should be noted in this connection that the monoammonium salt is formed when the diammonium salt decomposes and gives off ammonia. It is most likely that identical results would be obtained by using either of these salts; however, there may be some property of the diammonium salt, occurring when it decomposes that would aid the reaction.

III. Ammonium Acid Sulphate - NH_4HSO_4

$$Ca_3(PO_4)_2 + NH_4HSO_4 = 2CaHPO_4 + CaSO_4 + NH_3$$

While wet mixtures of superphosphates,

dolomite, limestone, or ammonium phosphate react to give a large proportion of the neutral $CaHPO_4$, the above process would have a tremendous economical advantage considering the relative cost of raw rock phosphate and superphosphate. (20)

There is an additional possibility:

$$Ca_3(PO_4)_2 + 3NH_4HSO_4 = 2NH_4HPO_4 + 3CaSO_4 + NH_3$$

Should this reaction proceed as indicated pure phosphoric acid of any concentration might then be obtained by low temperature thermal decomposition of the ammonium phosphate. The advantages over the furnace and wet methods for phosphoric acid can readily be appreciated.

There is still one other possibility. If the reaction between rock phosphate and ammonium acid sulphate is carried out in the presence of moisture it might proceed thus:

(1) $Ca_3(PO_4)_2 + 2NH_4HSO_4$ aq. $= CaH_4(PO_4)_2 + 2CaSO_4 + 2NH_4OH$

(2) $CaH_4(PO_4)_2 + 2NH_4OH = CaHPO_4 + (NH_4)_2HPO_4 + 2H_2O$

(3) $2CaSO_4 + (NH_4)_2HPO_4 = CaHPO_4 + CaSO_4 + NH_4HSO_4 + NH_3$

It is certain that the reaction shown under (1) above would take place for this is much the same reaction that is obtained by adding H_2SO_4. However, in this case the additional product $2NH_4OH$ is

formed. It is this product that would enable the reaction to continue to a more desired product.

This discussion and the theoretical equations show the processes that were investigated. To obtain the desired results would be a matter of untold importance to the fertilizer industry. A new process for manufacture of an improved and more economical fertilizer, both from the standpoint of the user and the manufacturer, would be opened. Such a process would add much to the value of Tennessee's natural wealth.

METHOD PURSUED IN MAKING INVESTIGATIONS

The method used in making these investigations was essentially the same for all cases. A weighed amount of ground rock phosphate was thoroughly incorporated with a weighed amount of finely ground ammonium salt. This mixture was then fused. The product obtained from the fusion was ground and an analysis was obtained. The results of the analysis were used to make calculations in order to determine the value of the reaction.

The procedure as described above was essentially what was done for all salts in all cases. However, there were several variables that entered into this simple procedure, and the effect of each of these variables needed to be determined.

For each ammonium salt used, the amount of salt was varied from the theoretical amount to as high as 300% excess of the theoretical amount. By making this variation, the most efficient amount of salt to use for the fusion was determined.

Another important variable was the condition under which the fusion was carried out. For each salt, fusions were made with the mixture in an open beaker at constant pressure, in a closed system at constant volume, in a closed system under a vacuum of 20 cm. of Hg, and in an atmosphere of steam. Results obtained by this

procedure served to indicate the conditions under which the fusion should be carried out in order to obtain the best results.

Perhaps the most important variable was the temperature at which the fusion was carried out. This had much to do with the result obtained. If an attempt had been made to run each different mixture under each condition at all temperatures, the combinations would have been so many that years might have been required to complete the work. However, test runs were first made, and a complete temperature range was run only for those mixtures and conditions which seemed promising.

Another variable that entered into the process was time. Time seemed to have little effect if the fusion was allowed to go until the reaction stopped; however, the length of time through which the reaction continued had to be determined for each case.

In general, the above was the method used in making these investigations. For each ammonium salt fused with the rock, it was attempted to determine the most economical amount of salt to use and under what conditions the best result was obtained. When these facts were known, a temperature variation was run on the mixture. By this procedure, the most economical amount of salt, the condition, and the temperature yielding the best result was obtained.

DESCRIPTION OF APPARATUS AND MATERIALS

Materials

The principal material necessary for these investigations was rock phosphate. The rock phosphate used was Tennessee Brown Rock. The rock had been previously ground to a particle size of approximately 80% through 200 mesh.

A generous supply of this rock was put through a sampling device and a representive sample was obtained. The representive sample thus obtained was analyzed and the remainder of the rock was put in a container and kept for use in making the investigations.

The analysis of the Tennessee Brown Rock Phosphate was:

P_2O_5	CaO	Fe_2O_3	Al_2O_3	SiO_2	CO_2
32.1%	44.5%	2.8%	1.3%	8.1%	2.0%

Rock of this analysis was used in all the investigations.

The ammonium salts used were all Baker's Analyzed, Chemically Pure compounds. The ammonium salts used were $(NH_4)_2HPO_4$, $NH_4H_2PO_4$, and NH_4HSO_4.

The rock and the salts were the only materials used other than distilled water.

Apparatus

I. Oven

In order to make the fusions between rock phosphate and various ammonium salts, heat had to be supplied by some means. The first method used for

supplying heat was by use of a small electric oven. This oven, having a volume of approximately one cubic foot, contained only one heating coil and had a maximum temperature of about 150 C. By thickening the walls of the oven with several sheets of asbestos paper, the heat losses were cut down and a maximum temperature of 200 C. was obtained.

The use of this oven was simple. The mixed sample, in its container, was placed in the oven and allowed to fuse for the desired length of time. It was necessary, however, to have the oven up to the desired temperature before introducing the sample and it was also necessary to control the temperature while the sample was in the oven.

Temperature control of the oven was difficult, except when operating at the maximum, and had to be done by manipulation of a switch. Although this oven did not give very accurate temperature control it could be regulated within ± 10 C. and the oven was found to be very valuable in carrying out these fusions due to the ease with which the samples could be run under all conditions.

II. Bomb

For making runs at constant volume, a small iron bomb was used. This bomb was made from a

six inch piece of No. 2 double extra strong iron pipe. A bottom was securely welded in and a screw top, made air tight by means of a lead gasket, was used to seal the bomb. This bomb had a volume of approximately 10 cu. in. Samples to be fused at constant volume were placed in a suitable container in the bomb, which was then sealed and put into the oven.

II. Vacuum Bomb

It was decided to try fusion of rock phosphare and ammonium salts under vacuum. For making these runs a small bomb was constructed from a short piece of flange pipe. A bottom was welded on and a top, made air tight by use of a lead gasket, was bolted on by means of bolts through the flange. A small $\frac{1}{4}$" pipe welded through the side of the bomb made vacuum connections possible.

The vacuum apparatus as constructed consisted of the vacuum bomb with vacuum line, containing a manometer and bleader valve, connected to a water vacuum pump. The apparatus was so constructed that the bomb could be placed in the oven with the vacuum line, which was connected to the $\frac{1}{4}$" pipe, coming out of a hole in the top of the oven. This bomb was so adjusted that a stream of air passed through it to carry off generated gases and thus prevent saturation. A standard procedure of fusion under a vacuum stream

of 20 cm. of Hg., referred to atmospheric pressure, was established for the vacuum runs.

IV. Constant Temperature Oil Bath

As previously stated, extremely accurate temperature control could not be obtained with the electric oven. When the fact was established that processes that did not require the use of bombs gave better or as good results as those processes requiring bombs, it was decided to discontinue the use of bombs.

For further investigations the need of a more accurate method of temperature control was realized. For accurate temperature control a constant temperature bath was decided upon.

A small tank 6 inches wide by 9 inches deep by 18 inches long was constructed of 20 gage sheet iron. This tank was used as the bath and the seams were welded water-tight. Since temperatures up to 200 C. were required, water could not be used. For this purpose a heavy cylinder oil, S. A. E. 50, was obtained and found to be very satisfactory. The flash point of this oil was well above the maximum temperature at which the bath was to be used.

For heating the bath an immersion coil was constructed. This coil was constructed of 'Chromel A' resistance wire and was calculated to heat the bath to 200 C. when operating on 110 volts. This coil

successfully heated the bath but caused smoking of the oil, due to the small heating surface and localized heating. Later this coil was replaced by two 220 volt, 750 watt commercial immersion heating coils. These coils, having a large heating surface, were permanently installed in the bath. The lead posts of these coils were brought out through the side of the tank and rigidly secured.

A small electric propeller type stirrer was used to insure complete mixing of the oil and secure a uniform temperature through out the bath. The temperature was regulated by means of a commercial Precision Temperature Regulator. This regulator consisted of a Thermostat Unit, which was immersed in the oil bath, connected to a Relay which in turn controlled the flow of current to the heating coils. By charging the Thermostat Unit with the correct sensitive liquid, very accurate control of temperature, over the desired range, could be obtained. (± 0.2 C.)

V. Steam Bath

For carrying out fusions in an atmosphere of steam the constant temperature oil bath was used. The mixture to be fused was placed in a beaker and the beaker was immersed about $\frac{3}{4}$ of its depth in the oil bath. A special cover, containing a steam connection, was used on the beaker.

Steam was generated by boiling water in a flask heated by means of an electric hot plate. The steam passed from the flask through a trap bottle, which served to remove any entrained water, then through a superheater coil. From the superheater the steam was fed to the bottom of the beaker and flowed out through an opening in the cover. The superheater was a small copper coil immersed in the oil bath. Its purpose was to heat the steam to the same temperature as the oil bath before it was supplied to the fusing sample. By means of this simple set-up a constant supply of steam was generated and fed to the fusing sample at the same temperature as the oil bath in which the sample was fusing.

DISCUSSION OF RESULTS

Results Obtained by Fusion of $(NH_4)_2HPO_4$ and Rock Phosphate

In table No. 1 is shown the complete set of runs made with rock phosphate and $(NH_4)_2HPO_4$. As shown by the table runs were made at constant pressure, constant volume, and in an atmosphere of steam. Temperature was varied from 150 to 200 C. with heating periods lasting from three to five hours. Twenty grams of rock was used in all cases and the amount of $(NH_4(_2HPO_4$ fused with the rock, was varied from 50% excess of the theoretical amount to 100% excess of the theoretical amount. (See appendix for all calculations) Results showed a C. I. ratio varying from 0.99 to 1.45. The C. I. ratio is obtained by dividing the grams of P_2O_5 in the rock charged by the grams of C. I. P_2O_5 in the product. This gives a good indication of the value of the reaction since all the P_2O_5, charged in the rock, is in the C. I. form. Ideal conditions would be when there was no C. I. P_2O_5 in the product. For this ideal case the C. I. ratio would equal infinity.

This data eludes all attempts at correlation and only general observations can be made. The best results were obtained when a mixture of rock and approximately 56% excess $(NH_4)_2HPO_4$ was fused in an iron bomb at constant volume. Here the C. I. ratio was 1.45 and indicates that 31% of the rock P_2O_5 was changed from the C. I. form. This is a very poor result

considering that a mol ratio of 2.54, (see appendix) as compared with the theoretical mol ratio of 1.81, was used. The mol ratio is the mols of $(NH_4)_2HPO_4$ divided by the mols of rock P_2O_5. This shows the relative amounts of rock and salt used for the fusion.

The results shown in table No. 1 indicate that W. S. P_2O_5 is being changed either to the C. S. or the C. I. form. In one case there is more C. I. P_2O_5 in the product than was present in the original mixture; and, in all cases there is less W. S. P_2O_5 in the product. This gives rise to difficulties in attempting to determine the value of the reaction. (See appendix)

In view of these difficulties, no attempt was made to calculate the % rock reacting, and the value of the reaction was expressed in terms of the C. I. ratio as previously discussed.

Summary of Results of $(NH_4)_2HPO_4$ Fusions

(1). The best product was obtained by fusion of 56% excess $(NH_4)_2HPO_4$ and rock phosphate at constant volume for five hours at 190 C.

(2). An atmosphere of steam hinders, rather than helps, the reaction and gives very poor results.

(3). Although better results are obtained when the reaction is carried out at constant volume, the

increase in conversion is very slight and is not enough to be appreciable.

(4). The use of a large percentage excess salt does not increase the reaction.

(5). Temperatures in the neighborhood of 200 C. are necessary for the fusion reaction with $(NH_4)_2HPO_4$.

(6). Results in no case show a desirable product. Only small amounts of the desired C. S. P_2O_5 were obtained with most of the available P_2O_5 being obtained in the W. S. form. This result could be obtained more cheaply, with complete reaction of the rock, by the use of acid.

(7). In no case do results indicate that the process would be economically feasible.

Results Obtained by Fusion of $NH_4H_2PO_4$ and Rock Phosphate

In Table No. 2 is shown the complete set of runs made with rock phosphate and $NH_4H_2PO_4$. As the table shows, runs were made under constant pressure, constant volume, vacuum, and atmosphere of steam. Temperature was varied from 150 to 300 C., with heating periods lasting from two to five hours. Twenty grams of rock was used in all cases and the amount of $NH_4H_2PO_4$ fused with the rock was varied from the theoretical to 100% excess of the theoretical amount. (See appendix) Results showed a C. I. ratio from 0.76 to 1.19. The C. I. ratio is the grams of rock P_2O_5 divided by the grams of C. I. P_2O_5 in the product as previously described.

In approximately half of these runs a C. I. ratio of less than one was obtained. This indicates that there was more C. I. P_2O_5 in the product than there was in the original rock and approximately the same situation exists as was discussed for the fusions with $(NH_4)_2HPO_4$. (Also see appendix.)

In order to obtain comparisons as to which condition was most favorable for the reaction, samples were selected, having the same mol ratio, under all conditions. Table No. 3 shows results of comparisons made on this basis. The samples shown in this table

have a mol ratio of 2.72 or 14.07 grams of $NH_4H_2PO_4$ to 20 grams of rock phosphate. This is 50% excess of the theoretical amount of $NH_4H_2PO_4$ required. Results of Table No. 3 are also shown graphically in figure No. 1.

As indicated by table No. 3 and figure 1, the highest C. I. ratio was obtained for the run made at constant pressure. However, this highest C. I. ratio was only 1.19 and indicates that only 15.7% of the rock P_2O_5 has been changed from the C. I. form. This is a very small amount, especially considering that a mol ratio of 2.72, as compared with a theoretical mol ratio of only 1.81, was used.

Even though the best results, with a mol ratio of 2.72, were obtained by fusion at constant pressure; there was only a very small increase in the C.I. ratio. The best results obtained, corresponded to only about 15% of the rock P_2O_5 being made available. In some cases part of the salt P_2O_5 was changed to the C. I. form, as previously discussed for fusions with $(NH_4)_2HPO_4$.

It is easily seen that fusions yielding no better results than these are not feasible, for none of the processes make enough of the rock P_2O_5 available to be of any practical value.

Summary of Results of $NH_4H_2PO_4$ Fusions

(1). The best results were obtained by

fusion at constant pressure using a mol ratio of 2.72.

(2). The effect of varying the proportion of the reagents was not noticeable.

(3). Approximately half of these fusions resulted in forming more C. I. P_2O_5 in the product than was put into the original sample.

(4). Only 15% of the rock P_2O_5 was changed to the available form in the best result obtained.

(5). Fusion processes with $NH_4H_2PO_4$ and rock phosphate, in the light of the results obtained, are impractical.

Results Obtained by Fusion of NH_4HSO_4 and Rock Phosphate

In Table No. 4 is shown the results obtained by fusion of NH_4HSO_4 and rock phosphate when the reaction was carried out in a bomb at constant volume. As shown by the table, the results indicate a favorable reaction. The amount of available P_2O_5 obtained in the product varies from approximately 75 to 85%. The formation of C. S. P_2O_5 seems to be favored by the lower temperature, for the greatest per cent of C. S. P_2O_5 was obtained at the lowest temperature employed and the highest temperature yielded the least.

It should be noted, in connection with ammonium acid sulphate fusions, that all the P_2O_5 in the mixture comes from the rock phosphate. Since NH_4HSO_4 contains no P_2O_5, all the P_2O_5 in the sample is added in the rock in the C. I. form. Analysis of the product gives an accurate indication of the amount of rock reacting, since any P_2O_5 occurring in any form other than the C. I. form has been changed by the fusion reaction.

The results of fusions made under a vacuum of 20 cm. of Hg. are shown in table No. 5. These results indicated that vacuum seemed to hinder rather than aid the reaction and yielded lower per centages of available P_2O_5 in the product. However, these results

did show that the extent to which the reaction took place depended much on the amount of NH_4HSO_4 used. Accordingly a standard mol ratio of 5.80 was established for future runs. (See appendix for excess reactant calculations.)

Table No. 6 shows the complete set of fusions made between NH_4HSO_4 and rock phosphate when a mol ratio of 5.80 was used. Fusions were made under all conditions at varying temperatures in an attempt to find the condition and temperature most favorable to the reaction.

In order to ascertain under which condition the best reaction was obtained, a run to represent each condition was selected from table No. 6. The result of this selection is shown in Table No. 7.

In Table No. 7 the run selected was the best result obtained for that particular condition. This was thought to be the best means of comparison, since the mol ratio is constant, and the most favorable temperature and heating period varies for each of the conditions. As indicated by the table, the best results were obtained when the fusion was carried out in an atmosphere of steam. Results of Table No. 7 are also shown graphically in figure 4.

Fairly good results were obtained on runs

made at constant volume; however, there was little investigation done along this line mainly because: (1) slightly better results could be obtained by using an atmosphere of steam. (2) cost of adequate equipment for use in carrying out constant volume runs was excessively high, It was felt that the added expense and complications were not justified since better results were obtained by some other method.

Table No. 7 further shows that the largest proportion of C. S. P_2O_5 was formed in the run made under constant volume. For this particular run this was true and this was the highest per cent of C. S. P_2O_5 that was formed in any case. This result was not typical for the constant volume runs and was peculiar to this one case. Other runs made at constant volume gave a smaller per cent of C. S. P_2O_5 as well as a larger per cent of W. S. P_2O_5. Taken as a whole the runs made in an atmosphere of steam gave the largest per cent of C. S. P_2O_5 and the highest per cent conversion.

Since it had been determined that fusions gave the best result when carried out in an atmosphere of steam, it was desired to determine the temperature most favorable to the reaction. In order to determine this a plot was made, from those runs of Table No. 6 which were made in an atmosphere of steam, of temperature

vs. the per cent of rock P_2O_5 available. This plot is shown in figure 1.

An examination of the data plotted, shows that no accurate curve can be drawn; however, a curve can be approximated. The approximated curve is shown on the sheet and indicates that 100% conversion os the rock P_2O_5 should be obtained at approximately 70C. Since this curve is only an approximation, no accurate information could be obtained from it; however, it does clearly indicate that the reaction between NH_4HSO_4 and rock phosphate, when carried out in an atmosphere of steam, is favored by the lower temperature.

When a mixture of rock phosphate and ammonium acid sulphate is heated to somewhat above 150 C. for a couple of hours, it becomes viscous and plastic. Upon further heating the mixture hardens to a dense compact body. It has been thought that more of the P_2O_5 of the rock would be changed to the available form if the mixture was stirred while in the plastic state. It was hoped that stirring would expose new rock surface to the fused salt for reaction. In order to determine the effect of stirring, several duplicate runs, one of which was stirred while the other was not, were made. Table No. 8 shows the result of this determination.

The two sets of runs shown in table No. 8 are identical except for the fact that all runs in one

set were stirred. All other conditions such as time, temperature, amount of NH_4HSO_4, and method used are identical for the two sets.

The only comclusion that can be drawn from table No. 8 is that stirring has no definite effect. The amount of rock P_2O_5 reacting, per cent P_2O_5 made W.S., and per cent made C. S. seems to be independent of whether the mixture is stirred or not. As is shown in the table, half of the runs show better results where the mixture was stirred while in the fluid state, and half the runs show better results where the mixture was not stirred. This indicates that stirring has no definite effect and that added complications and expense caused by stirring would not be warranted.

Since it had been established that the best reaction between NH_4HSO_4 and rock phosphate was obtained in an atmosphere of steam, it is shown that the presence of moisture is favorable to the reaction. In Table No. 6, when a mol ratio of 5,80 was used, the best results were obtained at 100 C. in an atmosphere of steam. When an atmosphere of steam was not used, no reaction could be obtained below the fusion point of NH_4HSO_4. Further investigations are confined to fusions carried out in an atmosphere of steam.

In Table No. 9 is shown results of fusions

between NH_4HSO_4 and rock phosphate when a mol ratio of 2.10 is used and the reaction is carried out in an atmosphere of steam. Here the mol ratio was reduced to 2.10 because the use of such large amounts of NH_4HSO_4 as previously used, would be too expensive for a practical process.

Since indications are that the presence of moisture is necessary, the reaction is evidently taking place according to the third set of equations as given for the reaction between NH_4HSO_4 and rock phosphate on page 11. Accordingly, for part of the fusions shown in Table No. 9, water was added to the mixture and it was made into a thick paste before being fused in an atmosphere of steam. Results obtained by this method gave very poor results as shown in table No. 9; however, these results were as good as the others listed in table No. 9, for the dry mixture fused in an atmosphere of steam. Taken as a whole, the results shown in this table are much poorer than those of table No. 6. This seems to indicate that the higher mol ratio of 5.80 is more favorable to the reaction than the lower mol ratio of only 2.10.

As previously discussed, Table No. 6 indicated that 100% conversion of the rock P_2O_5 might be expected at approximately 70 C. This fact was

investigated and the results of this work was incorporated in table No. 9. An examination of the runs which were made at 70 C. shows that 100% reaction is not obtained and that the runs made at this temperature seem no more favorable than most others. Figure 3, however, was obtained using a mol ratio of 5.80 so that the curve would not apply exactly to these runs.

Run No. 5483-K of Table No. 9 should be noted. The procedure used for this run was different from that used on any other run. In this case the mixture of rock and NH_4HSO_4 was placed in a flask and water was added to make a thin sludge. This sludge was mechanically stirred by a small propeller mixer and heat was supplied by heating the flask with a small bunsen burner. A reflux condenser was attached to the top of the flask to prevent the evaporation of water. The result obtained by this method was very poor and this procedure was not repeated. The bad results obtained for this case were most likely due to the presence of too much water.

A comparison of Tables No. 6 & 9 seems to indicate that the mol ratio has much to do with the reaction. An investigation was made to determine the effect of the amount of NH_4HSO_4 used. These results are shown in Table No. 10 and also.shown graphically

in figure 2.

Figure 2 was plotted from the data of table No. 10. This data was obtained by carefully selecting runs which were made using various mol ratios. An examination of this curve shows that the largest per cent of rock P_2O_5 was made available when a mol ratio of approximately 5.80 was used. For higher or lower ratios the curve drops sharply indicating that less rock P_2O_5 is made available. Figure 2 indicates that the best conversion of the rock P_2O_5 that we can expect to obtain is by use of a mol ratio of 5.80 with the fusion carried out in an atmosphere of steam.

Summary of Results of NH_4HSO_4 Fusions

(1). Best results were obtained by fusion in an atmosphere of steam; however, these results were only slightly better than those at constant volume.

(2). A curve drawn from data obtained from fusions in an atmosphere of steam and a mol ratio of 5.80 indicated that 100% conversion of the rock P_2O_5 might be expected at approximately 70°C.

(3). A mol ratio of 5.80 was found to give the best reaction. The use of either higher or lower mol ratios resulted in a smaller percentage of available P_2O_5 in the product. This fact is shown in figure 2.

(4). Stirring the mixture while in the

plastic state had no definite effect. The amount of rock P_2O_5 reacting, per cent made W. S., and C. S. is independent of whether the mixture is stirred or not.

(5). The best result obtained was approximately 85% available P_2O_5 in the product. This result was obtained by heating in an atmosphere of steam at 100 C., using a mol ratio of 5.80.

(6). Results are impractical since no better reaction than 85% conversion could be obtained and this by using a large mol ratio of 5.80. The use of this much NH_4HSO_4 would be more expensive than acid and results in a less desirable product.

Results Obtained by Heating H_2SO_4 and Rock Phosphate

It was suggested that the high conversion obtained by digestion of rock phosphate with ammonium acid sulphate might be due to the formation of acid from the decomposition of NH_4HSO_4. To compare the acid reaction with the salt fusions, several mixtures of rock phosphate and H_2SO_4 were treated in a manner similar to that employed for the rock ammonium acid sulphate fusions. The amount of H_2SO_4 employed corresponded to the acid in the NH_4HSO_4 when a mol ratio of 4.33 was used.

The results obtained from the H_2SO_4 runs is shown in table No. 11. These results cannot be compared very accurately with those obtained by the use of NH_4HSO_4. When H_2SO_4 is used, a large per cent of the P_2O_5 in the product exists as F. A. (Free Acid). This runs as high as 83% in cases where the reaction is complete.

The per cent of P_2O_5 in the product that is C. S. is slightly higher than that obtained by use of NH_4HSO_4 under constant pressure; however, at constant volume the per cent C. S. P_2O_5 almost disappears in the H_2SO_4 runs. This was not the case for NH_4HSO_4.

Whenever H_2SO_4 is added in sufficient quantity, the reaction will go to completion giving

a product having large amounts of F. A. and W. S. P_2O_5. In using the NH_4HSO_4, too large an amount of the salt resulted in decreasing the per cent P_2O_5 made available.

The results seem to indicate that, although accurate comparisons cannot be made, the reaction obtained by the use of NH_4HSO_4 is not due to its decomposition into acid and the results obtained in the two cases are not the same.

Summary of Results of H_2SO_4 Fusions

(1). Accurate comparisons cannot be made between the H_2SO_4 and NH_4HSO_4 fusions.

(2). The use of H_2SO_4 results in the formation of large percentages of free acid P_2O_5 in the product. None is obtained when NH_4HSO_4 is used.

(3). Complete reaction is obtained when sufficient H_2SO_4 is used. The use of too much NH_4HSO_4 decreases the reaction and complete reaction cannot be obtained.

(4). The results seem to indicate that the reaction obtained by the use of NH_4HSO_4 is not due to its decomposition into acid and that the results obtained by the use of H_2SO_4 are not the same as those obtained with NH_4HSO_4.

CONCLUSIONS

General Conclusions Reached from the Investigation

(1). All attempts to produce a product substantially corresponding to dicalcium phosphate by fusing rock phosphate with ammonium salts were unsuccesful to the extent that incomplete conversion of rock P_2O_5 (0 - 85%) and large proportions of water soluble P_2O_5 (0 - 68%) were invariably obtained.

(2). The best conversion of the rock P_2O_5 was obtained by fusing a mixture of NH_4HSO_4 and rock phosphate having a mol ratio of 5.80 at 100 C. in an atmosphere of steam for two hours. The per cent of the total P_2O_5 made available in this case was 84.8%. The C. S. P_2O_5 was only 24.7% of the total.

(3). In no case was a product obtained which corresponded largely or in whole to dicalcium phosphate.

(4). In all cases the conversion of the P_2O_5 was incomplete and even for these partial conversions the amount of salt that had to be used was excessive.

(5). On basis of the foregoing statements, the only logical conclusion that may be drawn is that such a fusion process would be impractical.

TABLE NO. 1

RESULTS OF $(NH_4)_2HPO_4$ AND ROCK PHOSPHATE FUSIONS

AMOUNT OF ROCK CONSTANT AT 20 GRAMS

No.	Temp. C.	Mol Ratio*	Total P_2O_5	% P_2O_5 in product that is: W.S.	C.S.	C.I.	C. I.# Ratio	Remarks
				Constant Pressure				
6463-K_1	155	2.54	15.71 G.	59.5	6.3	34.2	1.19	Heated 5 Hours
6463-K_2	155	2.54	15.71 G.	55.7	7.7	36.6	1.11	" " "
6459-K_1	185	2.54	15.71 G.	57.6	6.8	36.5	1.21	" " "
6459-K_2	185	2.54	15.71 G.	56.3	7.4	36.0	1.12	" " "
6459-K_3	185	2.54	15.71 G.	51.6	7.4	41.0	0.99	" " "
6481-K	200	2.43	14.22 G.	58.4	3.4	38.0	1.19	" " "
				Constant Volume				
6453-K	190	2.54	15.71 G.	46.7	22.1	31.2	1.45	Heated 5 Hours
6454-K	190	2.54	15.71 G.	48.4	18.5	33.1	1.39	" 3 "
6489-K	195	4.67	21.27 G.	46.2	28.1	25.7	1.17	" 5 "
				Atmosphere of Steam				
5480-K	200	2.45	14.22 G.	37.3	20.5	42.2	1.07	Heated 5 Hours

* Mol Ratio = $\frac{\text{Mols of } (NH_4)_2HPO_4}{\text{Mols of Rock } P_2O_5}$

\# C. I. Ratio = $\frac{\text{Gms. of } P_2O_5 \text{ in Rock Charged}}{\text{Gms. of C.I. } P_2O_5 \text{ in Product}}$ (All P_2O_5 in rock charged is C.I.)

TABLE NO. 2

RESULTS OF $NH_4H_2PO_4$ AND ROCK PHOSPHATE FUSIONS

AMOUNT OF ROCK CONSTANT AT 20 GRAMS

No.	Temp. C.	Mol* Ratio	Total P_2O_5	% P_2O_5 in product that is: W.S.	C.S.	C.I.	C. I.# Ratio	Remarks
				Constant Pressure				
6463-K_3	155	2.89	15.65 G.	51.2	8.0	40.8	1.00	Heated 5 Hours
6525-K	200	2.72	15.08 G.	33.4	30.3	36.3	1.19	" " "
5478-K	200	3.62	17.97 G.	64.2	6.1	29.7	1.19	" " "
6485-K	300	2.72	15.08 G.	12.8	39.6	47.6	0.89	" " "
				Constant Volume				
6484-K	300	2.72	15.08 G.	40.3	4.0	55.7	0.76	Heated 5 Hours
				Vacuum of 20 cm. of Hg.				
6480-K	155	2.72	15.08 G.	43.0	23.3	36.7	1.16	Heated 5 Hours
6478-K	175	1.81	12.19 G.	21.3	31.5	47.2	1.11	" " "
6483-K	200	2.72	15.08 G.	27.2	21.9	49.1	0.83	" " "
				Atmosphere of Steam				
6508-K	150	2.72	15.08 G.	54.8	6.1	39.1	1.10	Heated 2 Hours
6523-K	197	2.72	15.08 G.	43.1	10.2	47.2	0.92	" " "
6524-K	200	2.72	15.08 G.	38.9	11.6	50.5	0.85	" " "
5476-K	200	3.62	17.97 G.	55.7	8.9	35.4	1.00	" " "
5477-K	200	3.62	17.97 G.	53.7	4.1	42.2	0.84	" 5 "

* Mol Ratio = $\frac{\text{Mols of } NH_4H_2PO_4}{\text{Mols of Rock } P_2O_5}$

\# C.I. Ratio = $\frac{\text{Gms. of } P_2O_5 \text{ in Rock Charged}}{\text{Gms. of C.I. } P_2O_5 \text{ in Product}}$ (All P_2O_5 in rock charged is C.I.)

TABLE NO. 3

EFFECT OF CONDITIONS UNDER WHICH A MIXTURE OF $NH_4H_2PO_4$ IS FUSED WITH ROCK PHOSPHATE**

No.	Fusion Condition	Mol Ratio*	% P_2O_5 in product that is: W.S.	C.S.	C.I.	C. I. Ratio#	Remarks
6484-K	Constant Volume	2.72	40.3	4.0	55.7	0.76	Heated 5 Hours
6508-K	Atmos. of Steam	2.72	54.8	6.1	39.1	1.10	" 2 "
6525-K	Constant Pressure	2.72	33.4	30.3	36.3	1.19	" 5 "
6480-K	Vacuum, 20 cm. Hg.	2.72	43.0	23.3	36.7	1.16	" 5 "

* Mol Ratio = $\frac{\text{Mols of } NH_4H_2PO_4}{\text{Mols of Rock } P_2O_5}$

C.I. Ratio = $\frac{\text{Gms. of } P_2O_5 \text{ in Rock Charged}}{\text{Gms. of C.I. } P_2O_5 \text{ in Product}}$ (All P_2O_5 in rock charged is C.I.)

** See figure 3.

TABLE NO. 4

RESULTS OF NH_4HSO_4 AND ROCK PHOSPHATE FUSIONS

AT CONSTANT VOLUME

No.	Temp. C.	Mol* Ratio	Total P_2O_5	% P_2O_5 in product that is: W.S.	C.S.	C.I.	% P_2O_5 Available	Remarks
6456-K	180	4.83	6.4 G.	63.2	21.0	15.8	84.2	Heated 5 Hours
6467-K	155	5.66	6.4 G.	46.6	33.2	20.2	79.9	" " "
6469-K	300	5.66	6.4 G.	58.8	15.7	25.5	74.5	" " "

* Mol Ratio = $\frac{\text{Mols of } NH_4HSO_4}{\text{Mols of Rock } P_2O_5}$

TABLE NO. 5

RESULTS OF NH_4HSO_4 AND ROCK PHOSPHATE FUSIONS

UNDER 20 CM. VACUUM

No.	Temp. C.	Mol* Ratio	Total P_2O_5	% P_2O_5 in product that is: W.S.	C.S.	C.I.	% P_2O_5 Available	Remarks
6482-K	200	5.80	6.4 G.	52.9	20.3	26.8	72.4	Heated 5 Hours
6487-K	200	1.92	6.4 G.	8.4	10.3	81.3	18.7	" " "

* Mol Ratio = $\frac{\text{Mols of } NH_4HSO_4}{\text{Mols of Rock } P_2O_5}$

TABLE NO. 6

RESULTS OF NH_4HSO_4 AND ROCK PHOSPHATE FUSIONS

MOL RATIO IS CONSTANT AT 5.80*

No.	Temp. C.	Total P_2O_5	% P_2O_5 in product that is: W.S.	C.S.	C.I.	% P_2O_5 Available	Remarks
			Atmosphere of Steam				
6512-K	100	6.4 G.	68.1	24.7	15.2	84.8	Heated 2 Hours
6511-K	130	6.4 G.	68.2	7.6	24.2	75.8	" " "
6516-K	130	6.4 G.	62.3	0.0	41.1	62.3	" " "
6510-K	140	6.4 G.	65.3	11.6	23.1	76.9	" " "
6509-K	145	6.4 G.	63.0	12.2	24.8	75.2	" " "
6507-K	150	6.4 G.	58.0	11.5	30.5	69.5	" " "
6514-K	175	6.4 G.	61.6	10.7	27.7	72.3	" " "
6515-K	196	6.4 G.	57.4	14.2	28.4	71.6	" " "
			Constant Pressure				
6513-K	100	6.4 G.	-------No Reaction----------				Heated 2 Hours
6505-K	150	12.8 G.	60.2	7.5	32.3	67.7	" " "
6506-K	150	12.8 G.	40.9	25.3	33.8	66.2	" " "
6501-K	175	12.8 G.	44.1	6.5	37.0	63.0	" " "
6502-K	175	12.8 G.	56.5	7.5	32.3	67.7	" " "
			Constant Volume				
6467-K	155	4.8 G.	46.6	33.2	20.2	79.9	Heated 5 Hours
6468-K	300	4.8 G.	58.8	15.7	25.5	74.5	" " "
			Vacuum of 20 cm. of Hg.				
6482-K	200	6.4 G.	52.9	20.3	26.8	72.4	Heated 5 Hours

* Mol Ratio = $\frac{\text{Mols of } NH_4HSO_4}{\text{Mols of Rock } P_2O_5}$

TABLE NO. 7

EFFECT OF CONDITIONS UNDER WHICH MIXTURES OF ROCK PHOSPHATE AND NH_4HSO_4 ARE FUSED#

MOL RATIO IS CONSTANT AT 5.80 *

No.	Temp. C.	Fusion Condition	Total P_2O_5	% P_2O_5 in product that is: W.S.	C.S.	C.I.	% P_2O_5 Available	Remarks
6505-K	150	Constant Pressure	12.8 G.	60.2	7.5	32.3	67.7	Heated 2 Hrs.
6482-K	200	Vacuum, 20 cm. Hg.	6.4 G.	52.9	20.3	26.8	72.4	" 5 "
6467-K	155	Constant Volume	4.8 G.	46.6	33.2	20.2	79.9	" 5 "
6512-K	100	Atmosphere of Steam	6.4 G.	68.1	24.7	15.2	84.8	" 2 "

See figure 4.

* Mol Ratio = $\frac{\text{Mols of } NH_4HSO_4}{\text{Mols of Rock } P_2O_5}$

TABLE NO. 8

EFFECT OF STIRRING ON FUSION REACTIONS BETWEEN

NH_4HSO_4 AND ROCK PHOSPHATE *

No.	Temp. C.	Mol Ratio	% P_2O_5 in product that is: W.S	C.S.	C.I.	Available	Remarks
			Runs Stirred				
6505-K	150	5.80	60.2	7.5	32.3	67.7	Heated 2 Hours
6501-K	175	5.80	44.1	18.4	37.5	62.5	" " "
6516-K	130	5.80	62.3	0.0	41.1	62.3	" " "
6518-K	150	7.73	71.7	4.2	24.1	75.9	" " "
			Runs Not Stirred				
6506-K	150	5.80	40.9	25.3	33.8	66.2	Heated 2 Hours
6502-K	175	5.80	56.5	6.5	37.0	63.0	" " "
6511-K	130	5.80	68.2	7.6	24.2	75.8	" " "
6517-K	150	7.73	75.3	0.0	29.2	70.8	" " "

* All conditions other than stirring are the same for both sets of runs.

TABLE NO. 9

RESULTS OF NH_4HSO_4 AND ROCK PHOSPHATE FUSIONS

IN AN ATMOSPHERE OF STEAM

MOL RATIO IS CONSTANT AT 2.10*

No.	Temp. C.	Total P_2O_5	% P_2O_5 in product that is: W.S.	C.S.	C.I.	% P_2O_5 Available	Remarks
		Dry Mixture Fused in an Atmosphere of Steam					
5492-K	125	6.4 G.	21.4	17.4	61.2	38.8	Heated 3 Hours
5494-K	150	6.4 G.	21.9	13.1	65.0	35.0	" " "
5490-K	200	6.4 G.	15.1	12.4	72.5	27.5	" " "
	#	Wet Mixture Fused in an Atmosphere of Steam					
5488-K	70	6.4 G.	31.5	8.7	59.8	40.2	Heated 3 Hours
5487-K	70	6.4 G.	29.2	12.6	58.2	41.8	" 5 "
5496-K	100	6.4 G.	22.8	9.2	68.0	32.0	" 3 "
5483-K	100	32.0 G.	11.2	8.8	80.0	20.0	" 5 "
5493-K	125	6.4 G.	22.8	15.2	62.0	38.0	" 3 "
5495-K	150	6.4 G.	23.8	11.8	64.4	35.6	" 3 "
5489-K	175	6.4 G.	20.6	21.9	57.5	42.5	" 3 "
5491-K	200	6.4 G.	13.7	18.9	67.4	32.6	" 3 "

* Mol Ratio = $\frac{\text{Mols of } NH_4HSO_4}{\text{Mols Rock } P_2O_5}$

All runs listed under wet mixtures had water added to make into a paste except run No. 5483-K which was made into a thin sludge and heated by a flame. A reflux condenser kept water constant and it was stirred.

TABLE NO. 10

EFFECT OF THE AMOUNT OF NH_4HSO_4 USED IN NH_4HSO_4 AND ROCK PHOSPHATE FUSIONS WHEN CARRIED OUT IN AN ATMOSPHERE OF STEAM*

No.	Temp. C.	Ratio Mol	Total P_2O_5	% P_2O_5 in product that is: W.S.	C.S.	C.I.	% P_2O_5 Available	Remarks
5479-K	200	1.92	6.4 G.	9.5	12.1	78.4	21.6	Heated 5 Hours
5494-K	150	2.10	6.4 G.	21.9,	13.1	65.0	35.0	" 3 "
5497-K	70	4.33	6.4 G.	64.4	13.4	22.2	77.8	" 5 "
6512-K	100	5.80	6.4 G.	68.1	24.7	15.2	84.8	" 2 "
6518-K	150	7.73	6.4 G.	71.7	4.2	24.1	75.9	" 2 "

* These results shown graphically in figure No. 2.

TABLE NO. 11

RESULTS OBTAINED WHEN MIXTURES OF H_2SO_4 AND ROCK PHOSPHATE WERE TREATED SIMILAR TO METHOS EMPLOYED FOR ROCK-NH_4HSO_4 FUSIONS

No.	Temp. C.	Total P_2O_5	H_2SO_5 Gms.	% P_2O_5 in product that is: W.S.	F.A.	C.S.	C.I.	F.A. H_2SO_4 in product	% P_2O_5 Available	Remarks
				Constant Pressure						
6472-K	175	6.4 G.	21.3	42.7	34.1	23.2	o0.0	8.82 G.	100.0	Heated 5 Hr.
6473-K	"	6.4 G.	10.7	31.6	11.4	25.2	31.6	0.22 G.	68.4	" " "
6496-K	"	6.4 G.	10.5	8,0	14.7	55.0	22.3	0.24 G.	77.7	" " "
6498-K	"	6.4 G.	21.0	9.3	55.5	35.2	0.0	4.80 G.	100.0	" " "
				Constant Volume						
6474-K	175	5.7 G.	19.2	65.6	29.9	4.5	0.0	15.85 G.	100.0	Heated 5 Hr.
6475-K	"	6.3 G.	10.5	47.4	14.2	6.3	31.9	0.78 G.	68.1	" " "
6497-K	"	6.4 G.	10.5	22.5	26.1	7.3	44.1	0.00 G.	55.9	" " "
6499-K	"	6.4 G.	21.0	13.7	82.8	3.4	o.0	1.90 G.	100.0	" " "

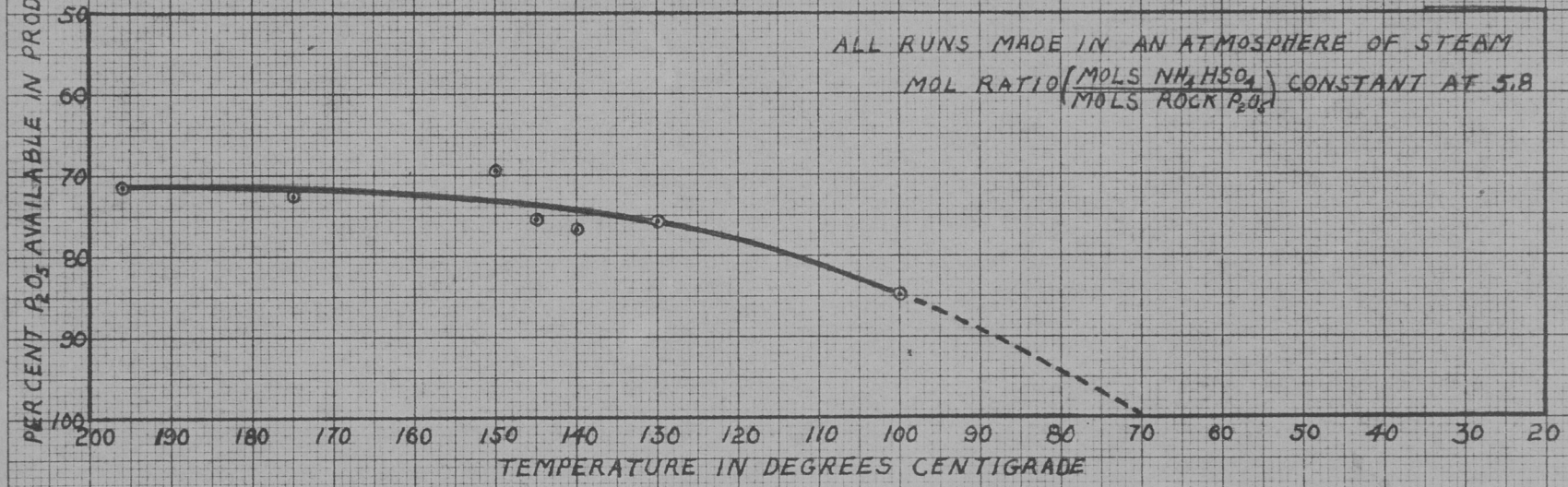


FIG. 1

EFFECT OF TEMPERATURE ON REACTION BETWEEN NH_4HSO_4 AND ROCK PHOSPHATE

Campbell

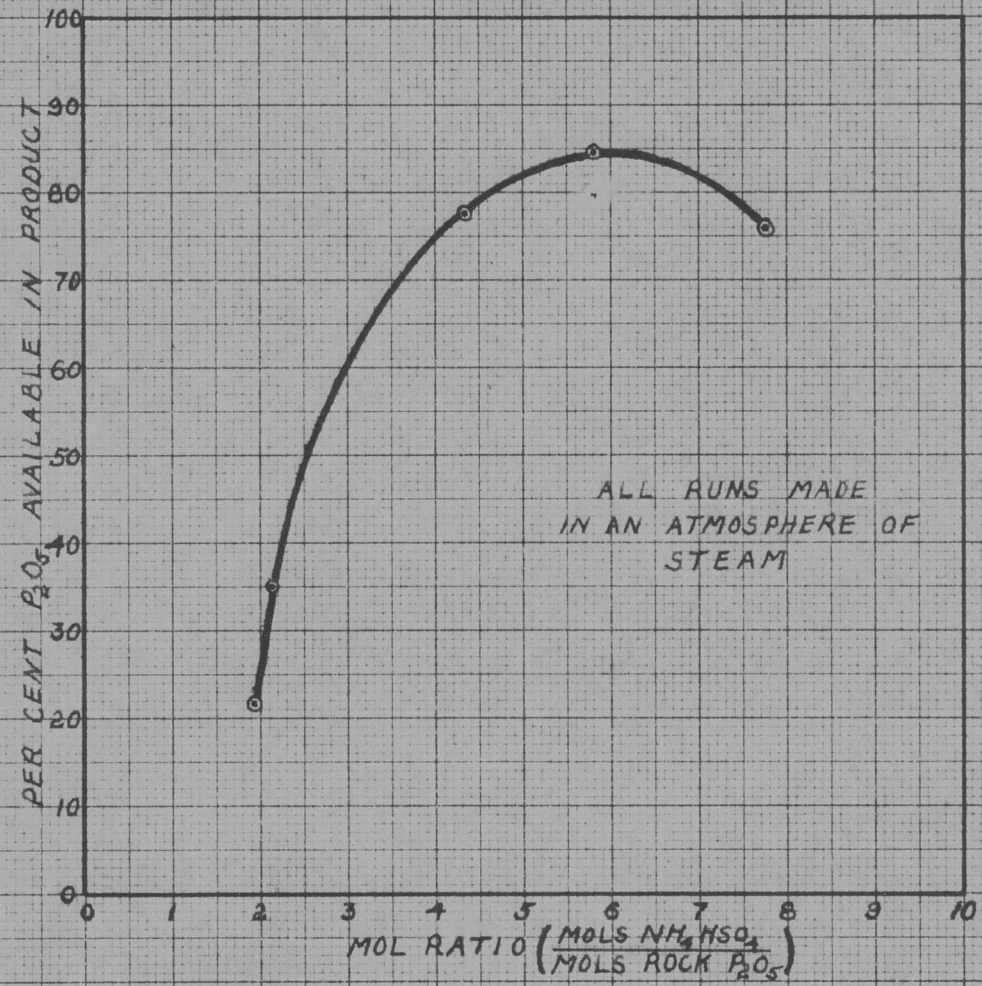


FIG. 2

EFFECT OF AMOUNT OF NH_4HSO_4 USED IN NH_4HSO_4 AND ROCK PHOSPHATE FUSIONS

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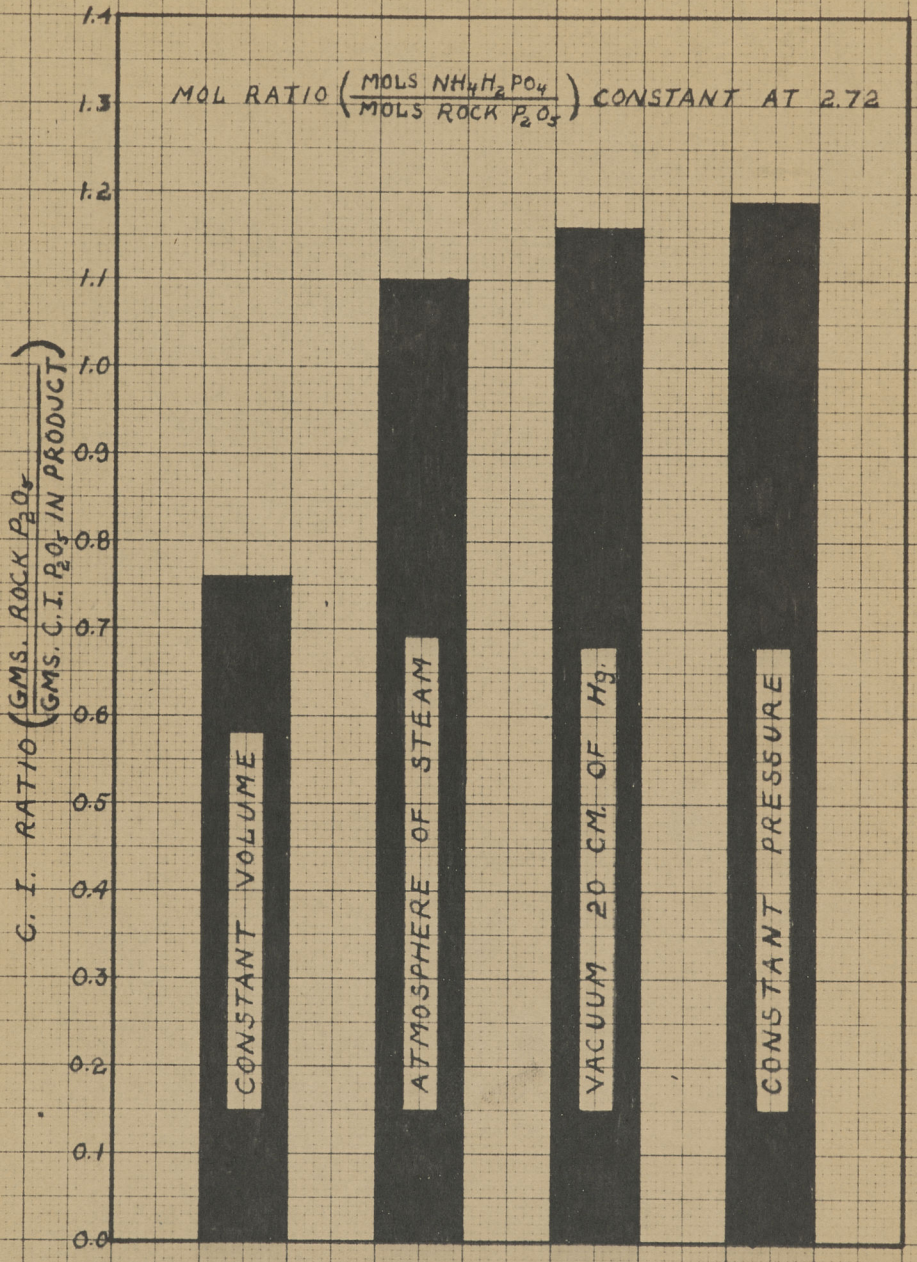


FIG. 3

EFFECT OF CONDITIONS UNDER WHICH MIXTURE OF $NH_4H_2PO_4$ AND ROCK PHOSPHATE ARE FUSED

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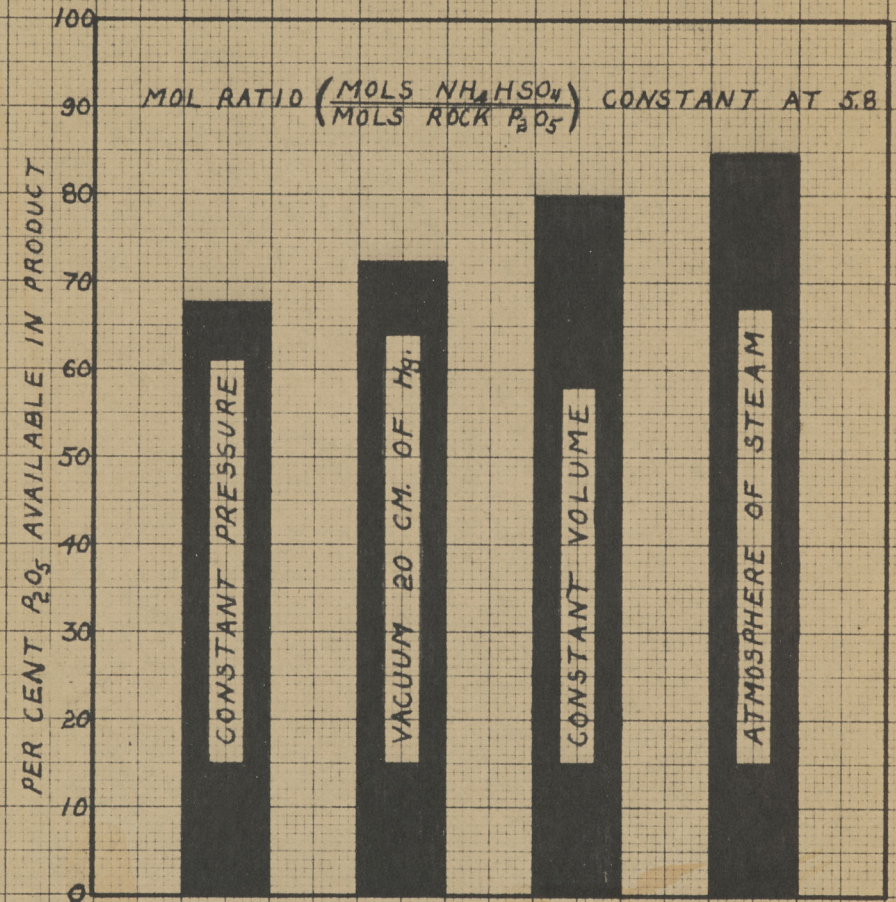


FIG. 4

EFFECT OF CONDITIONS UNDER WHICH MIXTURE OF NH_4HSO_4 AND ROCK PHOSPHATE ARE FUSED

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APPENDIX

Calculation of Theoretical Amount of $(NH_4)_2HPO_4$ Required

The amount of $(NH_4)_2HPO_4$ required to react with the rock phosphate was calculated from the rock analysis.

Analysis of Rock:

P_2O_5	CaO	Fe_2O_3	Al_2O_3	SiO_2	CO_2
32.0%	44.5%	2.8%	1.3%	8.1%	2.0%

The theoretical amount of $(NH_4)_2HPO_4$ necessary to react with rock phosphate is calculated according to the equations:

$$CaO + (NH_4)_2HPO_4 = CaHPO_4 + NH_4OH + NH_3$$

$$Fe_2O_3 + 2(NH_4)_2HPO_4 = 2FePO_4 + 3H_2O + 4NH_3$$

$$Al_2O_3 + 2(NH_4)_2HPO_4 = 2AlPO_4 + 3H_2O + 4NH_3$$

For a sample of 20 grams of rock phosphate, the theoretical amount of $(NH_4)_2HPO_4$ necessary is:

Mols of CaO present

$$\frac{20 \times .445}{56.1} = \text{------} \quad 0.1618$$

Mols of P_2O_5 needed for CaO

$0.1619/2 =$ ------- 0.0809

Mols of P_2O_5 in rock

$$\frac{20 \times .32}{142} = \text{-------} \quad 0.0452$$

Mols of Salt that must be added for CaO

$(0.0809-0.0452) \times 2 =$ 0.0714 --------- 0.0714

Mols of R_2O_3 in rock --- 0.0050

Mols of Salt that must be added for R_2O_3

0.0050×2 ---------- 0.0100

Mols of Salt to be added as $(NH_4)_2HPO_4$ = 0.0814

Weight of $(NH_4)_2$ = 0.0814×132 = ------10.75 Gms

This calculation shows the means by which the theoretical amount of $(NH_4)_2HPO_4$ necessary to react with 20 grams of rock phosphate was determined.

In order to obtain some basis for the expression of the relative amounts of $(NH_4)_2HPO_4$ and rock phosphate used, the mol ratio was set up.

The mol ratio is obtained by dividing the mols of $(NH_4)_2HPO_4$ used by the mols of rock P_2O_5.

Thus for the case where 20 grams of rock phosphate is treated with the theoretical amount, or 10.75 grams, of $(NH_4)_2HPO_4$ the mol ratio is:

Mols of $(NH_4)_2HPO_4$ = 10.75/132 ---- 0.0814

Mols of rock P_2O_5 = 6.4/142 ------- 0.0450

Theoretical Mol ratio = 0.0814/0.0450 --- 1.81

Sample calculation of Result Obtained from $(NH_4)_2HPO_4$ and Rock Phosphate Fusions

Run No. 6459-K_3

Twenty grams of rock was mixed with fifteen grams of $(NH_4)_2HPO_4$ in a beaker. The open beaker was placed in an oven and heated for five hours at 185 C. The product was then leached with water. The residue was dried and submitted to the laboratory for analysis.

The weight of the dried residue was 20.72 grams and it had an analysis:

Total P_2O_5	C. I. P_2O_5	CaO
36.7%	31.1%	42.1%

Calculations:

Input of P_2O_5:

P_2O_5 in rock ---- 20 x 0.32 -------- 6.4 gms.

P_2O_5 in $(NH_4)_2HPO_4$ -- 15 x 0.62 ---- 9.3 gms.

Total input of P_2O_5 ----------15.7 gms.

Output of P_2O_5:

Total weight of residue ----------20.72 gms.

Total P_2O_5 in residue - 20.72 x 0.367--- 7.60 gms.

W.S. P_2O_5(Dissolved in H_2O)-- 15.7-7.6 = 8.10 gms.

C.I. P_2O_5 --- 20.72 x 0.311 ---------- 6.45 gms.

C.S. P_2O_5 --- 15.7-(8.1 + 6,45) -------- 1.15 gms.

Assuming that all the C.I. P_2O_5 present in the product existed as unreacted rock, then the per cent rock reacting is given by the equation:

$$100 - \frac{\text{Gms. of C.I. } P_2O_5 \text{ in product}}{\text{Gms. of } P_2O_5 \text{ contained in rock}} \times 100$$

This assumption is not justified, however, for in some cases more C.I. P_2O_5 was in the product than in the original rock.

A calculation of the per cent rock reacting could also be made by assuming that all the W. S. P_2O_5 in the product came from the salt and existed as such in the original mixture.

The formula based on this assumption would be:

$$100 - \frac{\text{Gms. of W.S. } P_2O_5 \text{ in product}}{\text{Gms. } P_2O_5 \text{ charged in the salt}} \times 100$$

This assumption has no justification since it is very likely that some of the rock P_2O_5 is changed to the W. S. form by the fusion reaction.

Since there is no basis for either of the above assumptions, the per cent rock reacting cannot be accurately calculated.

In order to have an expression that would indicate the value of the results obtained by the reaction, the C. I. ratio was established. The C. I. ratio is the grams of rock P_2O_5 divided by the grams of C. I. P_2O_5 in the product. This ratio gives a good indication of the value of the reaction since all the P_2O_5 added in the rock is in the C. I. form. Ideal conditions would be a C. I. ratio equal to infinity.

For Run No. 6459-K3 the C. I. ratio is:

$$\text{C.I. Ratio} = \frac{6.40}{6.45} = 0.99$$

This ratio indicates that there is more C.I. P_2O_5 in the product than was charged in the original rock.

Calculation of the Theoretical Amount of $NH_4H_2PO_4$

The theoretical amount of $NH_4H_2PO_4$ necessary to react with rock phosphate is calculated according to the equations:

$CaO + NH_4H_2PO_4 = CaHPO_4 + NH_4OH$

$Fe_2O_3 + 2NH_4H_2PO_4 = 2FePO_4 + 3H_2O + NH_3$

$Al_2O_3 + 2NH_4H_2PO_4 = 2AlPO_4 + 3H_2O + NH_3$

If a sample of 20 grams of rock phosphate of the same analysis as before is used, the theoretical amount of $NH_4H_2PO_4$ necessary is:

Mols of CaO in rock -- $\frac{20 \times .445}{56.1}$ = ----- 0.1618

Mols of P_2O_5 needed for CaO = 0.1618/2 = 0.0809

Mols of P_2O_5 in rock -- $\frac{20 \times .32}{142}$ = ----- 0.0452

Mols of P_2O_5 to be added ---------- 0.0358

Mols of $NH_4H_2PO_4$ needed for CaO ---------- 0.0716

Mols of R_2O_3 in rock ---------- 0.0050

Mols of P_2O_5 needed for R_2O_3 ---------- 0.0050

Mols of $NH_4H_2PO_4$ needed for R_2O_3 ---------- 0.0100

Total mols of $NH_4H_2PO_4$ needed ---------- 0.0816

Weight of $NH_4H_2PO_4$ needed = 0.0816 x 115 = --- 9.38 gms.

Theoretical mol ratio = $\frac{0.0816}{0.045}$ = 1.81

Sample Calculation of Results Obtained from $NH_4H_2PO_4$ and Rock Phosphate Fusions

Run No. 6484-K

Twenty grams of rock phosphate was mixed with 14.07 grams of $NH_4H_2PO_4$. The mixture was placed in an iron bomb and heated for five hours at constant volume at 300 C. The product was ground and submitted

to the laboratory for analysis.

The analysis of the product was:

Total P_2O_5	W. S. P_2O_5	C.I. P_2O_5
46.0%	18.5%	25.6%

Calculations:

Input of P_2O_5:

P_2O_5 in rock -- 20 x 0.32 --------- 6.4 gms.

P_2O_5 in $NH_4H_2PO_4$ -- 14.07 x 0.617 - 8.68 gms.

Total input of P_2O_5 ---------- 15.08 gms.

Output of P_2O_5:

Total P_2O_5 in product -- 32.8 x .46 - 15.08 gms.

C.I. P_2O_5 in product -- 32.8 x .256 - 8.40 gms.

W.S. P_2O_5 in product -- 32.8 x .185 - 6.07 gms.

C.S. P_2O_5 in product -- 32.8 x .018 - 0.61 gms.

C. I. Ratio = $\frac{6.4}{8.4}$ = 0.76

Calculation of Theoretical Amount of NH_4HSO_4 Required

The theoretical amount of NH_4HSO_4 necessary to react with rock phosphate may be calculate according to the equations:

$$CaO + NH_4HSO_4 = CaSO_4 + H_2O + NH_3$$

$$Fe_2O_3 + 3NH_4HSO_4 = Fe_2(SO_4)_3 + 3H_2O + 3NH_3$$

$$Al_2O_3 + 3NH_4SO_4H = Al_2(SO_4)_3 + 3H_2O + 3NH_3$$

If a sample of 20 grams of rock phosphate is used, the theoretical amount of NH_4HSO_4 necessary for

the reaction is:

Mols of P_2O_5 present in rock -- $\frac{20 \times .32}{142}$ -- 0.0452

Mols of CaO present in rock -- $\frac{20 \times .445}{56.1}$ -- 0.1618

Mols of R_2O_3 present in rock ---------- 0.0050

Mols of SO_4 needed (0.1618 ± 0.015) ------- 0.1770

Total Mols of NH_4HSO_4 needed ---------- 0.1770

Weight of NH_4HSO_4 needed - 0.177 x 116 ---- 20.0 gms.

Theoretical Mol Ratio = $\frac{0.177}{0.045}$ = 3.93

The theoretical amount of NH_4HSO_4 necessary to react with rock phosphate may also be calculated according to the equations:

$$3CaO + P_2O_5 + NH_4HSO_4 = 2CaHPO_4 + CaSo_4 + NH_3$$

$$Fe_2O_3 + 3NH_4HSO_4 = Fe_2(SO_4)_3 + 3H_2O + 3NH_3$$

$$Al_2O_3 + 3NH_4HSO_4 = Al_2(SO_4)_3 + 3H_2O + 3NH_3$$

For a similar sample of 20 grams of rock phosphate, the theoretical amount of NH_4HSO_4 necessary for the reaction is:

Mols Of CaO in rock (as above) -------- 0.1618

Mols of P_2O_5 in rock (as above) -------- 0.0450

Mols of CaO reacting to form $CaHPO_4$ ------ 0.0904

Mols of CaO left to form $CaSO_4$ ---------- 0.0713

Mols of NH_4HSO_4 needed to the added for the formation of $CaSO_4$ ----------0.0713

Mols of R_2O_3 in rock ---------- 0.0050

Mols of NH_4HSO_4 to react with R_2O_3 ----------0.0100

Total mols of NH_4HSO_4 needed ----------0.0863

Weight of NH_4HSO_4 needed = 0.0863 x 116 = 9.93 gms.

$$\text{Theoretical Mol Ratio} = \frac{0.0863}{0.0450} = 1.92$$

For the NH_4HSO_4 and rock phosphate fusions there are two possible theoretical mol ratios. Each is correct for its separate equations. The one that is correct for the fusion reaction depends on the manner in which the reaction proceeds.

Sample Calculation of Results Obtained from NH_4HSO_4 and Rock Phosphate Fusions

Run No. 6482-K

Twenty grams of rock phosphate was mixed with thirty grams of NH_4HSO_4. The mixture was put in an iron bomb and heated for 5 hours at 200 C. under a vacuum of 20 cm. of Hg. The product was ground and submitted to the laboratory for analysis. The weight of the fused product was 47.80 grams.

The analysis of the product was:

Total P_2O_5	C. I. P_2O_5	W. S. P_2O_5
13.8%	3.7%	7.3%

Calculations:

Output of P_2O_5:

C.I. P_2O_5 in product - 47.8 x .037 -- 1.77 g.

W.S. P_2O_5 in product - 47.8 x .073 -- 3.49 g.

C.S. P_2O_5 in product -(6.4 -(1.77+ 3.5) = 1.14 g.

Input of P_2O_5:

P_2O_5 in rock -- 20 x 0.32 ------ 6.4 g.

Per cent rock reacting = $100 - \frac{1.77}{6.4} \times 100 = 72.4\%$

Here, as for all the NH_4HSO_4 runs, the per cent rock reacting can be calculated. There is no P_2O_5 in the NH_4HSO_4; therefore, all the P_2O_5 in the mixture comes from the rock phosphate. Any P_2O_5 in the product in any form other than the C.I. form, has been changed from the original rock by the fusion reaction. Thus, with all the P_2O_5 coming from the rock phosphate, very accurate calculations of the amount of rock reacting can be made for the NH_4HSO_4 fusions.

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 does 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 C. F. Galloupe

Title Instructor