M. M. Austin

Potash in Illinois Shales
POTASH IN ILLINOIS SHALES

BY

MINER MANLY AUSTIN

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M. A. University of Illinois, 1918

THESIS

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY
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In Charge of Thesis

Head of Department

Recommendation concurred in*

Committee on Final Examination*

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The writer takes this opportunity to express his most sincere thanks and appreciation to Professor Parr for the valuable help and direction which he has given.

The writer also wishes to thank Dr. F. W. DeWolf, Professor T. E. Savage, and Professor Robert Stewart for the assistance which he has received from them.
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I GENERAL INTRODUCTION

Previous to 1914 the world's supply of agricultural potash came from the Stassfurt deposits in Germany. Table I shows our importations of potash material for 1914. All of this importation may be considered as coming from Germany.

The potash in these deposits occurs as the soluble minerals, Kainite \((K_2SO_4 \cdot MgSO_4 \cdot MgCl_2 \cdot 6H_2O)\), Carnallite \((KCl \cdot MgCl_2 \cdot 6H_2O)\), and Polyhalite \((K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O)\). Mixed with these minerals are three others which carry no potassium. They are Halite \((NaCl)\), Kieserite \((MgSO_4H_2O)\) and Anhydrite \((CaSO_4)\). The material is removed from the ground by shaft mining and the potassium is obtained in a commercially pure state by simple methods of crystallization. The production and marketing is completely controlled by the Kali Syndicate, which is itself a government subsidiary. Until the exploration of similar formations in Alsace, most of which has been done since 1914, no deposits were known which possessed such natural and commercial advantages. Their skillful exploitation has made it possible to meet and, in most cases, to crush all competition.

The abrupt decline in the importation of potassium material from 266,150 tons \(K_2O\) in 1914 to 86,380 tons in 1915 \((1)\), and then to almost nothing in 1916 created, in America, what appeared then to be a very grave economic problem. It was impossible to predict when relief might be expected, at the same time the necessity of supplying, as soon as possible, the demand for potash for agricultural purposes was fully realized. The rise in price
<table>
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<th>Kind</th>
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<td>$240451</td>
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<td>Chloride</td>
<td>263039</td>
<td>7925781</td>
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<td>Hydrate (crude)</td>
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<td>336650</td>
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<td>589245</td>
<td>2579619</td>
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<tr>
<td>Sulphate</td>
<td>50384</td>
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from $46 per ton $\text{K}_2\text{O}$ in 1914 to $\$351$ in 1918 (1) made available sources of supply in this country which were not workable before due to excessive cost of production. The net result was, therefore, the opening up of a number of new sources of potash as well as a marked increase in the activity of producers whose plants were already in operation. Although many of the projects that have been entered upon have not been successful, a fair proportion seem certain to continue as profitable enterprises. Some of the sources that have been developed, especially those in which potassium is recovered as a by-product, were entirely new and unanticipated and would never have been discovered except under the stimulation of the high prices that have prevailed. Although the details regarding the nature and methods of recovery in each of the producing and prospective sources are interesting, all that is in order here is a brief enumeration, together with a statement as to their possibilities and limitations. Table II gives the data on production of potash in the United States in 1918.

The saline lakes (3) (4), as will be noted from Table II, are yielding over three-fourths of the production of the United States at the present time. Operations are being carried on principally in two localities, one in northwestern Nebraska, and the other on Searles Lake in California.

The Nebraska deposits (3) consist in brine soaked sands which underlie the hard-pan at the bottom of shallow lakes. The brines contain from two to fourteen percent solids of which eight to thirty-six percent is potassium material calculated as
<table>
<thead>
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<th>Total Production</th>
<th>Available Potash (H₂O)</th>
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<tr>
<td></td>
<td>1917</td>
<td>1918</td>
<td>1917</td>
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<td>27</td>
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<td>4</td>
<td>7153</td>
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<td>12</td>
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<tr>
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<td>10</td>
<td>18</td>
<td>11306</td>
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<tr>
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<td>4</td>
<td>8</td>
<td>8589</td>
</tr>
<tr>
<td>Steffins Waste Water</td>
<td>5</td>
<td>51</td>
<td>2542</td>
</tr>
<tr>
<td>Wood Ashes</td>
<td>49</td>
<td>7</td>
<td>1035</td>
</tr>
<tr>
<td>Other Sources</td>
<td>6</td>
<td>9</td>
<td>2778</td>
</tr>
<tr>
<td>Total</td>
<td>95</td>
<td>126</td>
<td>126961</td>
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</table>
The pumping and evaporating operations necessary to recover the potash have not presented any great difficulty. The salt mixture obtained by direct evaporation of the brine is suitable, without further treatment, for use as fertilizer. To arrive at some conclusion as to the amount of material which this locality may be expected to yield, the results of a survey of Jesse Lake is cited. This lake which is the richest of the group is estimated to contain 250,000 tons of $K_2O$. This quantity is a little less than that imported into this country in 1914.

The formation at Searles Lake (4), California, is made up of a mixture of sodium and potassium carbonate, sulphate, and chloride, and some borax intermingled with more or less earthy material. The potash content is usually less than five percent, which suggests at once that the recovery of concentrated potassium salts is going to be expensive. Note also the additional fact that heavy transportation charges will have to be added to the cost of production, if material from this source is to be marketed in the central or eastern states. The advantages claimed for these deposits are the almost unlimited supply of raw material, and the possibility of large scale production.

Kelp (5), according to the statistics given in Table II, ranked second in quantity of production in 1918. Eighteen producers, all on the Pacific Coast were operating on this material. Among this number special reference should be made to the operations of the Hercules Powder Company (6), which is recovering iodine, calcium acetate, plastic material, filter carbon and a number of organic esters, along with potassium chloride of
ninety-five percent purity.

The kelp potash situation may be summarized in a few statements. Raw material is available only along the Pacific Coast, and there only in limited amount. Efforts to transplant to the Atlantic Coast have been unsuccessful. Harvesting has presented some difficulties which have, however, been quite completely overcome. Recovery of the potash is inherently expensive due to the large amount of water which must be evaporated. The problem of marketing is the same as that for material from Searles Lake. The possibility for elaborate by-producting processes such as worked out by the Hercules Powder Company speak in favor of the industry.

Alunite (7), the basic potassium aluminium sulphate, \( (K_2SO_4 \cdot Al_2SO_4 \cdot 4Al(OH)_3) \), though not producing as much potash as some other sources is to be regarded as of considerable importance due to its possibilities of development. Considerable quantities of this material have been located by the United States Geological Survey, in the neighborhood of Marysvale, Utah (8). The average potash content of alunite is ten percent. It may be recovered as commercially pure potassium sulphate by simply grinding, igniting at 1000°, and leaching. The residue remaining after leaching consists of fairly pure and finely divided Alumina. Its utilization as a by-product may become an important factor in the successful development of an alunite industry. It would seem that the principal reason why alunite has not been more extensively worked is that the deposits are inaccessible.

Molasses and distillery waste may be passed by with the
simple statement that their dependence upon the sugar industry makes then incapable of great extensions.

Wood ash (9), though one of the oldest sources of potash, will continually become less important as the supply of hard wood diminishes.

Blast furnace dust as a starting point for potash production, a suggestion that has been followed quite energetically in England (10), has also been the subject of some discussion in America and has been taken up in considerable detail by R. J. Wysor of the Bethlehem Steel Company (11). The theory involved is simply that the alkalis which enter the blast furnace with the charge are volatilized and carried out with the exit gases from which they may be recovered by dust precipitating operations. Observations made by Wysor indicate that these theories are practical. Claims have been made (11) that blast furnace dust might be developed in such a way as to supply one-third of our potash requirement. It seems doubtful, however, that such a claim will ever be realized. Analyses of iron ores (12), fluxes, etc., indicate that the best field of operation in this line would be on the smelters where Alabama ores are used, since these ores are characterized by a relatively high potash content.

Potash from cement dust (13) is a subject which has been given wide-spread publicity, as well as one on which much constructive research work has been done. Because of its direct bearing on the special problem under consideration the subject will be taken up in some detail.

That potash might become a by-product from portland cement
manufacture seems first to have been suggested in 1913 by F. G. Cottrell in an address before the New York meeting of the American Institute of Mining Engineers. In February of that year he reported the results of some of his work on the abatement of the dust nuisance at the Riverside Portland Cement Company plant, and mentioned incidentally as a matter of interest that the dust collected contained a considerable amount of soluble potash. Since that time the idea has been taken up by a number of cement companies and is now quite fully developed. The Riverside Cement Company of California and the Security Cement Company of New Jersey have been the most active in working out this by-product process.

The general theoretical considerations involved in the production of potash from cement are simple. At the temperature reached in the kiln, the potash which the raw material contains is volatilized and passes out as a fume with the burned gases. The dust and fume is precipitated from these gases by some appropriate means and the potash is leached from it with hot water.

The principal improvements that have been added since the idea was first taken up have been the use of salt or calcium fluoride to increase the proportion of potash volatilized (14); the use of hot instead of cold water in the leaching operation to break up the insoluble double calcium-potassium sulphate (15); improvement in the apparatus used in the electrostatic precipitation of the fume (16); and the designing of a type of wet washer to be used in place of the Cottrell apparatus (17).

The potash content of raw cement material has been investi-
gated by the United States Department of Agriculture and is reported in its Bulletin No. 572. Their work (18) has consisted in the determination and tabulation of the potash content of the clays, shales and limestones that are being used by over one hundred plants throughout the country. The only fact of interest that has been brought out in this report is that the raw mix now being used by American cement plants runs quite uniformly below one percent in potash. No other work seems to have been done along this line.

It is evident that for any yield of potash from cement manufacture, a reasonable amount of that element must be present in the raw material. An investigation which might lead to the discovery of cement material higher in potash than that now in use would be of value. The problem would have special interest locally because of lack of proximity to other potash supply, and because of the fact that the cement industry is well developed in a number of localities in the State.
II ILLINOIS SHALES

The shales of Illinois have been under investigation in this laboratory for some time. In 1916-17 and 1917-18, T. O. Westhafer (19) examined samples from a number of deposits in different parts of the State with special reference to their value for oil production. Along with a number of deposits of inferior material, he found one which showed, on distillation, a yield of 45.1 gallons of tar per ton (19). Although this latter shale is to be regarded as of technical interest for its tar yield alone, most of the samples examined cannot be so considered, and their utilization would require the discovery of other values in them. If other values were found to be present, not only would the shales of low tar yield come into the field of possible technical utilization, but interest would be added to those of high tar yield as well. It was not possible for Mr. Westhafer to go into this phase of the problem and in the fall of 1918 under Professor Parr's direction it was taken up by the writer as a separate piece of research.

The elements of value which one might hope to find in such material are very limited. Phosphorus, which has been found in some western shales (20), is absent in these as was shown by some preliminary tests. The nature of the material suggests its possible value for the manufacture of cement or ceramic products, but since ordinary clays and shales are abundant, the shales under study would need to contain some extraordinary values in order to have any special advantage. General interest in potash and especially potash as a by-product in the cement industry directed
attention toward their potash content. The fact that many of the shales contained considerable carbonaceous matter, which might become a fuel factor in the burning of cement, was also considered. As a result of this combination of circumstances the problem has developed into a general study of potash in Illinois shales.

At the beginning the work was confined quite closely to a determination of the potash content of the shales, and to their adaptability to cement manufacture. Later, however, shale was found which contained 5.0 percent of potash (21). Since this factor is higher than would have been expected in an Illinois shale (22), and compares favorably with material that has been worked primarily for its potash content (23), some experiments were carried out in the spring of 1913 to determine the type of chemical combination of the potassium as a preliminary step towards its possible commercial utilization. The work up to this point was written up in the spring of 1918 and presented as a Master's Thesis (21). The present investigation is a continuation of this work in which the distribution of these high potash shales, and some of their properties and commercial possibilities have been determined.
III REVIEW OF THE LITERATURE

In the course of a complete review of the literature, record of little work either practical or scientific has been found which has any very direct bearing on the problem in hand. The general subject of potash and potash sources has been thoroughly treated. To illustrate, the United States Geological Survey has published over seventy papers on potash from silicate rocks (24). Most of this work, however, relates to the utilization of feldspar and has been of little value to us.

Previous work, the results of which have been used in the present investigation will be taken up under the following headings:

1. Potash from cement
2. Specifications for cement material
3. The determination of rock constituents
4. Potash from feldspar
5. Alum shales
6. Spontaneous oxidation of coal pyrite
7. Leucite
8. Glauconite
9. Plant availability of potash material

1. Potash from Cement

Our interest in establishing the value, as cement material, of the shales which we have studied occasions the following summary of the earlier work on potash and cement.

Reference has already been made (18) to the work of Ross, Merz and Wagner, who studied the potash content of 113 American
cements and the raw mixtures from which they were made. They found that the average potash content of these raw mixtures ran quite uniformly under one percent and that on the average 47 percent of this potash was volatilized in the cement burning process. H. E. Brown (25) has patented processes for the utilization of feldspar, or other high potash material, in cement manufacture. Recent literature contains a number of references to the possibility of increasing the yield of potash from cement by using high potash shale, clay, or feldspar.

The Security Cement and Lime Company (26) has increased the proportion of potash volatilized in its kilns from 38 to 65 percent of the total in the raw mix by the use of one percent of common salt. Huber, Reath and Treavor (27) use fluorspar, which aids in the volatilization of the potassium from the raw mix by forming the more volatile potassium fluoride. When the gases cool off on leaving the kiln the potassium fluoride reacts again with the calcium salts which are also present in the dust in such a way as to reform the calcium fluoride and leave the potassium in a soluble condition. In the leaching operation the calcium fluoride which is insoluble remains in the sludge and is returned again to the kilns. This process is said to be in operation at the plant of the Riverside Portland Cement Company. It has been the experience of all of the cement plants that have given attention to the matter, that hard burning or burning at a high temperature increases the amount of potash volatilized. Aside from the improvements mentioned above, no change in the cement making operation is necessary in order to insure the presence of
most of the potash in the fume passing from the kilns.

F. G. Cottrell (38) in 1913, as has been previously noted, was the first to attempt the precipitation of the fume from cement plants. His method, which has been successful from the beginning, consists in the application of his now well-known system of electrostatic precipitation. The apparatus which he used at that time consisted of a group of vertical tubes down through the center of which wires were suspended. By means of transformers and mechanical rectifiers a direct current potential of 20,000 to 30,000 volts was maintained between the wires and the tubes. As the fume containing gas was conducted up through these tubes, the solid particles were thrown to the walls by reason of the electrostatic conditions existing there. By jarring of the tubes, and by cutting off the potential, the dust was made to fall down into collecting bins. J. J. Porter (39) reports an improvement which has been added to the apparatus which is in use at the plant of the Security Cement and Lime Company. At this plant a film of water is caused to flow down over the electrodes. This water carries the dust away continually and effects the solution of most of the potash at the same time. By bringing the water back over the electrodes several times a fairly concentrated solution is obtained. Porter also suggests the use of a preliminary settling chamber in which most of the coarser dust is removed. In this way a product of higher potash content is obtained from the precipitators. Where water film electrodes such as described above are used, the sludge which collects is digested at one hundred pounds steam pressure in order to remove
the potassium salts which it still contains. The reason for this latter operation will be considered further on. J. G. Dean (17) describes an interesting experimental plant that is being tried out at the Victorville, California, plant of the Southwestern Portland Cement Company. It is well known that an ordinary spray is not effective in removing finely divided suspended matter from gases. In this process the gases from the kiln are saturated with water vapor and then cooled until a mist is formed. The dust particles act as nuclei and must, therefore, be carried down with the mist. The heat which must be extracted from the gases before the moisture will condense is used in the concentration of the potash solution. For this purpose a sort of vacuum evaporator is used in which the hot gases are passed through tubes surrounded by a solution which is boiling under vacuum.

Nestell and Anderson (15) have investigated the nature of cement mill potash. They were led to look into this matter because of the fact that certain concerns were having difficulty in obtaining as much potash as they should from the dusts that they collected. They found that the potassium extracted is practically in the form of the sulphate, but that in some cases, where coal is used as fuel, that a double calcium potassium sulphate is formed which is insoluble in cold water. Hot water has been found to break up this double salt and is required, therefore, in the efficient extraction of the potash from the dust.

2. Specifications for Cement Material

A. V. Bleininger (23) has summarized in a concise manner the
general specifications which cement shales must meet. He considers the chemical composition of the clays or shales from the following standpoints:

1. Ratio between the percentage of silica and alumina
2. Magnesia
3. Ferric oxide
4. Sulphur
5 Alkalies
6 Inert mineral matter

The silica-alumina ratio in a cement mix is to be regarded as an important factor. The analysis of a number of good American cements shows that their average silica-alumina ratio is 2.9. The allowable limits have been set at 2.5 to 3.5. This factor is of course dependent upon the composition of the limestone as well as the clay that is to be used, but since most limestone is fairly pure it can be said with fair assurance that a shale with a ratio falling within these limits would be satisfactory.

The magnesia content in a finished cement ought not to be higher than three percent. Since this factor may run up rather high in the limestone, it should be low in the shale as a general rule.

Ferric oxide in a cement shale is desirable, since it promotes vitrification. Six to eight percent is not objectionable.

Sulphur is objectionable and should not be allowed to run beyond three percent in the finished cement. Since the fuel and the gypsum both contribute to the sulphur in the final pro-
duct, its presence in the shale should be in limited amount.

Alkalies cannot be considered objectionable since they act as a flux and lower the burning temperature.

"Inert mineral content" is the term applied to the percentage by weight of the residue which remains behind after the unground clay is intimately mixed with eight times its weight of calcium carbonate, heated to bright red heat, cooled, treated successively with hot hydrochloric acid and sodium carbonate solutions, and the residues finally washed thoroughly with a weak acid solution, and ignited. This process closely imitates the cement burning process and the residue is a measure of the amount of material which is too coarse to be attacked by the limestone. It is noted that in the case of shales the material will usually be so fine grained as not to leave an appreciable residue.

The principal physical property that should be possessed by a cement shale is a sufficiently fine grained and soft texture as to be easily ground.

Shales in particular, according to Bleininger, are as a class desirable for cement manufacture providing their chemical composition comes within the allowable limits. Table III gives the analysis of nine Illinois shales, most of which are suitable for cement making purposes.

3. The Separation and Identification of Rock Constituents

Since the first element in the problem of the utilization of these shales would seem to be the determination of their mineral constitution, what little literature has been found relating to this subject is given here.
### TABLE III (22)

#### Analyses of Illinois Shales

<table>
<thead>
<tr>
<th>Location</th>
<th>Silica (SiO₂)</th>
<th>Alumina (Al₂O₃)</th>
<th>Ferric Oxide (Fe₂O₃)</th>
<th>Ferrous Oxide (FeO)</th>
<th>Lime (CaO)</th>
<th>Magnesia (MgO)</th>
<th>Potash (K₂O)</th>
<th>Soda (Na₂O)</th>
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<td>15.43</td>
<td>1.80</td>
<td>4.02</td>
<td>0.93</td>
<td>1.58</td>
<td>3.28</td>
<td>0.56</td>
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<td>1.79</td>
<td>2.90</td>
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<td>6.74</td>
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</table>
Hillebrand in his treatise "The Analysis of Silicate and Carbonate Rocks" enumerates the following methods for the separation and identification of rock mixtures: Panning, upward flow of water, heavy solutions, magnetic susceptibility, and microscopic examination. He does not go into detail, and no other work has been found which gives a systematic method which is applicable to the shales under study.

The rational analysis for clay substance, feldspar and free silica as outlined by Mellor, "Treatise on Quantitative Inorganic Analysis" has been applied although the results which it gives are of doubtful significance.

Without reference to other work a number of determinations on relative solubility in acids have been carried out.

4. Potash from Feldspar

Although the material in hand is certainly not all feldspathic and more likely contains but a small amount of feldspar, the enormous amount of work that has been published on potash from this source might be expected to yield some valuable suggestions. Since the feldspars are the most refractory of the potassium minerals, one might expect that reagents which would attack them would also attack material such as shales. An additional reason for referring to the work on feldspar is that the shales which we have studied probably do contain smaller or larger amounts of this mineral.

No attempt is made here to cover all or even a small part of the work that will be found in the literature on potash from
feldspar. We are simply citing a sufficient number of references to indicate the general methods of attack that have been used.

The first general method to be considered is that in which the rock is heated with limestone and either a chloride, sulphate, fluoride or some other substance that will form a readily soluble alkali salt. It will be noted that this is the principle involved in the well known method of J. Lawrence Smith for obtaining total potash in silicate rocks.

F. O. Ward and F. Wynant (30) as early as 1857 proposed a method using feldspar, fluorite and chalk.

Rodin (31) was one of the first to propose the use of salt, limestone and feldspar.

Cushman and Coggesshall (32) have devised a method using feldspar, lime and salt which is said to give a product containing as much soluble potash as wood ashes. They mix 100 parts of feldspar rock with 30 parts of lime, and 30 parts of rock salt, and form the powder into small pellets by spraying a solution of calcium chloride on to the powder as it is being rolled in a revolving drum. About 20 parts of calcium chloride per 100 parts of feldspar is added in this pellet forming operation. The calcium chloride reacts with the lime to form an oxy-chloride which acts as a cementing material in forming the pellets. These pellets are then heated at a temperature of from 700 to 900 degrees in a rotary kiln such as used in the burning of cement. Fifty-five percent of the potash in the feldspar is said to be made soluble in this way. It is claimed that by this pelleting operation a sort of colloidal condition which exists in such a
mass of finely powdered material is overcome and that all of the particles are brought into intimate contact. It is also claimed that the calcium oxychloride is more easily dissociated than calcium chloride alone and is more effective in converting the potassium into the chloride. They have carried out the operation in lots of several tons and have tried out their product as fertilizer. However, the process does not seem to have been developed on a commercial scale, and, even if their claims are correct, is probable to be regarded as too expensive even under existing conditions of the potash market.

Cowles (33) describes a process which he has devised in which coal is added to a mixture similar to that described above and claims in that way to be able to liberate the potash.

Hart (34), Friedenburg (35), Quinney (36) and others proposed similar methods.

Methods in which the potash is recovered by volatilization seem to be so closely linked up with the work done along that line in connection with cement manufacture as to require no further discussion. A. J. Swayze (37) however, has patented a method which it would seem is capable of development. He proposes using feldspar, limestone and coke in a furnace similar to the blast furnace. The potash which is volatilized is precipitated from the exit gases. The temperature used is high enough to melt the charge and convert it into a slag which is drawn off, granulated in water and ground for cement. If such a process is practical from other standpoints it is to be noted that, since
complete fusion is brought about the raw materials would not have to be ground so fine as that required in the ordinary methods of cement manufacture.

Quite a little work has been done in studying the actions of lime under steam pressure on feldspars and other silicates. C. F. Hagedorn (38), C. H. MacClure (39), T. R. Ernest (40), W. R. Williams (41), A. W. Beemer (42) and F. L. Roman (43) all working in this laboratory have developed a number of phases of the problem. The first four workers mentioned above were interested primarily in the theoretical and practical aspects of the subject as it is related to the manufacture of sand-lime brick.

Mr. Roman (43) was the only one taking part in this work to give attention to the extraction of potash by this method. He found that by heating a mixture of equal parts of lime and feldspar for five hours at from 35 to 32 atmospheres steam pressure he could obtain thirty-five percent of the potash in the feldspar in soluble form.

Perhaps a more significant fact that has been discovered by these men is that when an attempt is made to cause lime and a silicate to react in this way, a sort of a capsule of a calcium aluminium silicate forms around the particles which seems to greatly inhibit the completion of the reactions.

William H. Ross (44) studied the action of lime on feldspar and obtained complete decomposition by heating equal parts of lime and feldspar in a metal bomb at 300° C. This temperature corresponds to a pressure of ninety atmospheres, which is obviously higher than could be used in autoclaves on a commercial basis.
Rose also found that, using a mixture of one part of feldspar to 1.7 parts of lime at ten atmospheres, eighty-five percent extraction could be obtained. The addition of calcium sulphate, nitrate or chloride and to a less extent sodium chloride increased the percent of potash extracted. When these salts were used the potassium was liberated as the corresponding salt, whereas if lime alone was used the potash was obtained as the hydroxide.

5. Alum Shales

The alum shales which have been used in former times as a source of material for the manufacture of aluminium sulphate have a bearing on this work since they seem to be identical in character with those under study. They are described as bituminous shales of the Silurian or Devonian formation containing finely divided iron pyrite.

Unfortunately little work either practical or scientific has been done on this type of material. Large books on inorganic chemistry, such as Roscoe and Schorlemmer describe the process used for obtaining aluminium sulphate from them, but give no details and treat the subject mainly for its historical interest. The method for working the shale was first to dig it out, pile it in heaps and expose it to the weather. In the course of a few months the pyrite was more or less completely oxidized to ferrous sulphate and sulphuric acid, both of which reagents attacked the shale in such a way as to yield aluminium sulphate. This aluminium sulphate was leached out and crystallized as an alum. In earlier times ammonium compounds were used to form the alum but later potassium sulphate came into use for this purpose.
It is to be noted that the process was one for the manufacture of aluminium sulphate and that the potassium sulphate was obtained from other sources and used simply to bring about the crystallizations of the less soluble potash alum. No mention is made of the fact that the shales might have contained some potassium which would undoubtedly be made soluble and appear along with the aluminium in the final product.

6. Spontaneous Oxidation of Coal Pyrites

The possibility of oxidizing to ferrous sulphate and sulphuric acid, the pyritic sulphur known to be present in many of the shales under study and to utilize these reagents to effect the decomposition of the shale had occurred to us, even before we had referred to the discussion on alum shales. Unfortunately no rapid method for oxidizing pyrite to the sulphates was known which could be applied experimentally to the shales. The only suggestions came through observations that have been made on the behavior of coal pyrite.

It is a fact quite commonly observed that coal piled in the open may become covered with a coating of white ferrous sulphate. The conditions which promote this reaction are not known. Professor Parr (45) has called attention to the fact that there is a marked tendency toward oxidation of pyrite even in coals contained in tightly stoppered sample bottles. One case is cited where a considerable quantity of ferrous sulphate was found in the bottom of a bottle in which a finely ground sample of coal had been contained for eight or ten months. Moisture seems to promote the oxidation, and the reaction also seems to proceed quite
rapidly after once started. Beyond this nothing is known which would indicate a method for bringing about the oxidation except by a weathering process.

7. Leucite

Leucite is an igneous rock which when pure is found to have the formula $\text{KAl(SiO}_3\text{)}_2$. It is found in lava flows where there is less silica present than would be required to form an orthoclase feldspar. Large deposits of the mineral occur in the Vesuvius district and deposits of considerable extent have now been located in this country (50). From the igneous origin of leucite it is evident that it could not occur as such in a shale that had undergone decomposition. The fact that it is more easily decomposed than feldspar and that for this reason quite a little work has been done in attempting to extract potash from it, makes it necessary to refer to some of this work here.

A. H. Rogers (51) has gone over most of the work that have been proposed for the utilization of leucite and has repeated quite a little of it in connection with some government investigations. He summarizes the properties of the mineral as follows:

1. In contrast to feldspar, leucite is easily decomposed.

2. When decomposed by wet acids, it yields its silica in granular form, differing in this respect from most silicates.

3. Sulphuric acid with a little hydrochloric acid completely dissolves the bases, but the salt mixture thus obtained is very difficult to separate.
4. Lime and gypsum gave a quantitative extraction of potassium sulphate.

5. Under just the right conditions lime may be used to take practically all of the potassium and aluminium into solution and leave the other metallic impurities in insoluble form. For this purpose the lime in proper proportion is mixed with the powdered leucite and the mixture heated in a cement kiln. The potash and aluminum can be leached from the ground clinker in a practically pure condition. The alumina can be precipitated from this solution either by passing in carbon dioxide or by a sort of catalytic method in which the aluminate is decomposed by the addition of alumina.

6. Extraction of potash from leucite is not practical unless it is possible to recover a by-product such as alumina.

3. Greensand

Greensand is a potassium bearing mineral occurring in considerable quantity in New Jersey and in some of the other eastern states (23). The mineral (61) is the potassium iron silicate known as Glanconite, but is never found in a pure condition. The material has attracted attention as a source of potash because it contains about seven percent of that constituent. It is not so refractory as feldspar, is fairly widely distributed along the Atlantic Coast and is easily mined. Two distinct methods of attack which might prove applicable to the shales have been found in the course of a review of the literature relating to greensand.
These suggestions are that such material may be of value when applied directly as fertilizer or that it may be attacked by lime in such a way as to bring the potash into solution.

A. Plant availability of greensand

R. H. True and F. W. Geise (46) have reviewed the literature relating to the value of greensand when applied directly as a fertilizer and also report the results of some of their own work. According to these authors greensand was used as a fertilizer over one hundred years ago, and was applied quite extensively about the time of the Civil War. However, a little or none has been used in late years.

True and Geise tried greensand as a source of potassium for the fertilization of clover and wheat growing in sand and fed by a standard plant food solution made up of potassium dihydrogen phosphate, calcium nitrate and magnesium sulphate. They conclude that plants are able to obtain potash from raw ground greensand.

J. G. Lipman and A. W. Blair (47) report results similar to those obtained above. They found that the results were less marked where an impure greensand was used.

B. Action of lime on greensand

W. H. Charlton (46) has used lime under pressure to obtain potash from greensand. He has found the material much less resistant than feldspar toward lime and has been able to get seventy to eighty percent extraction by heating at 200 to 250 pounds pressure for from two to four hours. He proposes to use the residue from which the potash has been leached as a binder for
sand lime brick.

Very recently an account has been published (49) of the activities of the Eastern Potash Corporation of New York. This corporation is erecting a large plant on the Raritan River Canal near New Brunswick, designed apparently to operate under the patents of W. H. Charlton. They expect to handle 1000 tons of greensand a day and produce 20,000 tons of potash and 600,000 tons of residue per year. They are constructing the largest lime plant in the world which comprises ten $3 \times 125$ rotary kilns which will have a capacity of 1000 tons of lime per day. The company is also intending to use its residues in the manufacture of sand lime brick and is constructing a plant for this purpose. They intend to make 1000,000 brick per day. The plant is now (April 23, 1920) sixty percent completed and is expected to be in operation in the early fall.


For some time past E. E. DeTurk (52) working with Professor Stewart has been carrying on an investigation in which he has studied the relative plant availability of potash material, such as orthoclase, microcline, leucite, alunite, muscovite, and lepidolite. Mr. DeTurk has been particularly interested in determining the effect of decaying organic matter, such as hay, alfalfa, and manure on the solubility if these minerals. This work has shown that some relatively insoluble minerals, leucite for example, are quite effective as potash fertilizers. In conjunction with this work, Professor Stewart, on learning of the shales that had come to light as a result of this investi-
igation, asked that he be furnished with some of the shale for the purpose of comparing its value as a potash fertilizer with the other materials that they had used. The material was furnished and the tests carried out. The results are as yet unpublished, but it may be said that they are very interesting and invited a continuation of the work, using similar experimental methods. With the cooperation of the Department of Agronomy we have carried the work on just a little farther in an effort to explain the peculiar results obtained by Professor Stewart.
IV EXPERIMENTAL

The different phases of the experimental work carried out in the course of this study will be treated in approximately the following order:

1. Samples
2. Analytical methods
3. Cement making possibilities of Illinois shales
4. Data relating to the constitution of Southern Illinois and Dixon shale and their relative stability as compared with feldspar
5. The action of various solid reagents on the shales
6. The action of various liquid reagents other than milk of lime
7. The action of lime under steam pressure on Southern Illinois shales
8. Plant availability of potassium in treated and untreated shale

1. Samples

The samples of shale used in this work were, unless otherwise stated, obtained through the Illinois State Geological Survey. Samples Nos. 1, 2, 3 and 4 were taken by F. W. DeWolf in the fall of 1918. It is not known who collected sample No. 5. Samples Nos. 6, 7, 8, 9 and 12 were taken by T. E. Savage in the summer and fall of 1919. Samples Nos. 10 and 11 were taken by E. A. Holbrook about January, 1917. Samples Nos. 102, 106, 107, 114, 115 and 116 were collected in 1917 and 1918 for Mr. Westhafer and designated by him as Nos. 3, 6, 7, 14, 15 and 16 (19).
Samples Nos. 1, 2, 3, 4, 6, 7, 10, 11 and 12 were taken on Caney Creek in Union County on the farm owned by H. C. Grear. The deposit is located south of the railroad track and three miles N. W. of Jonesboro, in S. W. 1/4, Sec. 11, T 12 S, R 2 W, 3rd P. M. on N. W. bank of this creek going S. W. These samples will be referred to hereafter as from the Caney Creek deposit.

Plate I shows the localities from which the shales were obtained.

Plate II shows the appearance of the best outcrop on Caney Creek. These photographs were taken by the author, who inspected the deposits at Caney Creek and State Pond in the spring of 1920.

Sample No. 1. About 5 pounds taken on Caney Creek represents the top 4 feet of greenish gray shale. It is immediately under four feet of limestone and is probably not commercially available in great amount.

Sample No. 2. About 5 pounds represents the bottom 4 feet of the same shale body as No. 1.

Sample No. 3. About 5 pounds represents the bottom 2 feet of the black paper shale on Caney Creek at the only spots where it is obtainable comparatively fresh and clean.

Sample No. 4. About 12 pounds in quartered from 35 pounds representing 8 feet of shale next above No. 3. It is badly weathered. Samples No. 3 and 4 are from the same section as No. 10, taken previously by Holbrook and sample No. 6 taken by Savage.
MAP OF ILLINOIS SHOWING LOCALITIES FROM WHICH SHALE SAMPLES WERE TAKEN
PLATE II

PHOTOGRAPHS OF SHALE OUTCROP ON CANEY CREEK
Sample No. 5. About eight ounces is a green sandy shale said by DeWolf to have been sent from near Dixon, Illinois, for examination as to potash and phosphorus content.

Sample No. 6. About 90 pounds represents the basal 8 feet of the black shale on Caney Creek.

Sample No. 7. About 80 pounds represents the section for 12 feet above that sampled in No. 6. The material is badly weathered.

Sample No. 8. About 50 pounds was taken from the lower 20 feet of a black shale formation outcropping near State Pond and about two miles north-west of Jonesboro. In that which follows, this deposit will be spoken of as the State Pond deposit.

Sample No. 9. About 40 pounds is taken from the upper 30 feet of black shale deposit, 1/2 mile S. W. of Mountain Glenn, and is to be referred to as from the Mountain Glenn deposit.

Sample No. 10. About 40 pounds is a section of the lower 10 feet of the deposit on Caney Creek. It, with sample No. 11 which follows, constitute the first sample that has been taken of this deposit.

Sample No. 11. About 40 pounds taken from the upper 25 feet above that represented by sample No. 10.

Sample No. 12. About 35 pounds taken from the upper 15 feet of the black shale on Caney Creek about 15 rods east of the point where sample Nos. 6 and 7 were taken.

Sample No. 102. Taken in Schuyler County in the S. W. 1/4, Sec. 23, T 2 W, R 1 W. Two feet of carbonaceous shale above
coal No. 5.

Sample No. 106. Sample of cannel coal or oil shale taken in Johnson County, N. W. 1/4, Sec. 35, T 11 S, R 4 E. Forty-two inch bed samples at outcrop.

Sample No. 107. The same as No. 106, except that it was taken by sampling a twenty-ton pile that had been mined and dumped beside the outcrop.

Sample No. 114. Taken in Moultrie County near Lovington. Black roof slate from top of Coal No. 6.

Sample No. 115. Sample taken from new shaft in same locality as No. 107. In this case a 1500-pound sample was taken about 1/4 mile from the outcrop.

Sample No. 116. Shale from a slag dump at a mine at Lincoln, Illinois. This sample was furnished Mr. Westhafer by a student, Ralph Gale. A more exact description is not available.

2. Analytical Methods

The analytical work involved in the carrying out of this research has been unusually difficult. The determination of potash in the shales themselves has called for a modification of the procedure that is usually applied to such material. Complete rock analyses, in so far as such have been made, have also been carried out in a manner slightly different from the ordinary. Various solutions and solid products have had to be analyzed and have each required special, and often time consuming, procedures in order that the results be fairly reliable. In the analysis
of these solutions and other products, it has not been possible to verify their accuracy experimentally. Every precaution has been taken to eliminate error which might arise from elements and conditions known to exist in these products, but beyond this, results which looked reasonable were assumed to be correct. Determination were made in duplicate, except in a few cases which will be noted.

In practically all cases, duplicates checked within five percent. Where greater variation then this occurred, redeterminations were made.

Qualitative tests for potassium were of no value since the element was always present in more than traces, yet never in large amounts.

The reagents used were Baker's Analyzed Chemicals, or others of equivalent grade and were usually obtained in the original unopened bottles. Except in cases where a blank is ordinarily run with an analysis or where observation leads us to suspect the purity of reagents, they were assumed to be pure enough for our purposes.

The following is an outline of our analytical procedure:

(a) Moisture and Ignition Loss

A five gram sample contained in an eight centimeter porcelain milk dish was dried at 105-110° for one hour. The loss was considered as free moisture. For ignition loss the dried sample was heated in the milk dish until all of the carbon had been burned away. The heating was gentle at first, but finally the bottom of the dish was brought to a low read heat. A few samples were
heated to constant weight, but we were soon able to tell by the disappearance of the carbon when the ignition was complete. The shale was stirred from time to time with a Nichrome wire.

The reason for using the five-gram sample was that sufficient ash was desired on which to run further analyses. To check up on the accuracy obtainable from such a procedure, a one-gram sample was ignited in an ashing dish. The percent of ash was found to be the same whether the smaller or larger sample was used.

(b) Potash and Soda

In the first of our work we were interested in the residues from the distillation of oil shales and for that reason we ashed down these shales by the method described and then conducted the total potash determinations on the ash. Later when working on shales which were only slightly carbonaceous, we attempted to use the raw shale in these determinations. However, the reducing action of the organic matter which was present in practically all of our material seemed to cause fusion of the J. Lawrence Smith charge. This made it stick to the crucibles and left it in such a condition as to disintegrate very slowly. We went back, therefore, to our old method of using the ash instead of the raw shale and used the ash factor to calculate the percent of potash in the raw material.

The actual determinations as has been indicated were made by the J. Lawrence Smith method. All of the precautions were observed. Platinum crucibles of the ordinary form were used for cintering the sample with calcium carbonate. Berlin porcelain
casseroles were used where the solution is first evaporated to dryness and the ammonium salts are driven off. Berlin porcelain evaporating dishes about nine centimeters in diameter were used to receive the solution of the pure chlorides. The precipitation with chlorplatinic acid and the subsequent operations including the final weighing were carried out in these dishes. Wells (53) and others working in this laboratory have found this method of handling the total chlorides quite satisfactory.

Chlorplatinic acid was used in obtaining all of the total potash factors for the shales, and was also used in most of the other determinations. Where perchloric acid was used the fact will be noted and the method of using it will be described.

In order to check our accuracy in these potash determinations a Bureau of Standards sample of shale was obtained from the Department of Analytical Chemistry. It was analyzed at two different times, using two different lots of chlorplatinic acid, which were made up for this work. Analyses were:

<table>
<thead>
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<th>2nd Analysis</th>
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</thead>
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<td>1.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.11</td>
</tr>
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</table>

Soda was calculated by difference from the weight of the total chlorides and the weight of potassium chloride known to be present.

**(c) Silica**

Silica was determined by the ordinary method of fusion with sodium carbonate and dehydration of the silicic acid by evaporation with hydrochloric acid. The recommendation by Hillebrand

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(54) that the solution be evaporated a second time after the main part of the silica had been filtered off was not observed. The volatilization of the silica by means of hydrofluoric acid was always carried out and the correction for non-volatile residue always applied.

(d) Ferric Oxide and Aluminia

Ferric oxide and alumina were separated from the solution from which the silica had been filtered by first adding to this solution a few drops of bromine water and then adding it to an excess of dilute ammonia. The first precipitate of iron and aluminium hydroxides was dissolved in nitric acid and reprecipitated in the manner described above. In igniting the second precipitate the ordinary precautions were observed regarding completeness, reduction, etc.

Ferric oxide in this precipitate was determined by dissolving it with fused sodium pyrosulphate, then reducing in slightly sulphuric acid solution with twenty mesh zinc and titration with tenth normal potassium permanganate.

(e) Calcium Oxide

Calcium was precipitated as oxalate in the filtrate from the iron and alumina. Since the amount of calcium always was small, only one precipitation was made and the calcium was determined simply by dissolving this precipitate in hot dilute sulphuric acid, and titrating with tenth normal potassium permanganate.

(f) Magnesia

To obtain the magnesia the filtrate from the calcium oxalate
was acidified, concentrated somewhat, and then the magnesium was precipitated by means of sodium ammonium hydrogen phosphate. The ordinary precautions regarding the stirring, addition of ammonia and concentration of ammonia in the final solution were observed. Care was also taken to wash the precipitate with ammonium nitrate solution and to ignite it in the proper way.

(g) Sulphate Sulphur, Pyritic Sulphur and Nitrogen

These factors were determined on a few samples. The method of obtaining them will be taken up later.

3. Cement making possibilities of Illinois shales

In considering the shales which we have examined for their cement making possibilities, we have relied principally on their chemical analysis and general physical character as compared with that which a cement shale should have. In drawing our conclusions, we have been guided by the discussion of cement material by A. V. Bleininger (22), which has been taken up in our review of the literature.

Table IV gives the analyses of Illinois shales which we have made. Table V gives the silica-alumina ratio, the calculated percentage of potash in the raw mix such as would have to be made for these shales, and the estimated amount of potash recoverable per barrel of cement.

We have arrived at the percentages of potash in the raw mix by using a simple formula for finished cement proposed by Michallis (56) and said by Bleininger (22) and Meade (57) to approximate fairly closely the compositions obtained in practice.
### TABLE IV

**Analysis of Illinois Shales**

<table>
<thead>
<tr>
<th>No.</th>
<th>Ash</th>
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<td>0.4</td>
<td>0.8</td>
<td>3.5</td>
<td>0.4</td>
</tr>
<tr>
<td>116</td>
<td>85.0</td>
<td>54.8</td>
<td>19.9</td>
<td>7.7</td>
<td>4.0</td>
<td>2.3</td>
<td>3.9</td>
<td>1.3</td>
</tr>
<tr>
<td>1</td>
<td>96.9</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>2</td>
<td>97.7</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>3</td>
<td>86.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>4</td>
<td>88.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>97.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>88.1</td>
<td>61.0</td>
<td>20.2</td>
<td>6.6</td>
<td>0.8</td>
<td>2.0</td>
<td>5.65</td>
<td>0.6</td>
</tr>
<tr>
<td>7</td>
<td>87.1</td>
<td>63.3</td>
<td>18.7</td>
<td>6.9</td>
<td>0.4</td>
<td>1.7</td>
<td>5.58</td>
<td>0.5</td>
</tr>
<tr>
<td>8</td>
<td>89.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>86.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>87.3</td>
<td>61.5</td>
<td>18.7</td>
<td>6.5</td>
<td>0.9</td>
<td>1.8</td>
<td>5.7</td>
<td>0.6</td>
</tr>
<tr>
<td>11</td>
<td>85.5</td>
<td>66.0</td>
<td>17.8</td>
<td>6.5</td>
<td>0.2</td>
<td>1.3</td>
<td>5.0</td>
<td>0.7</td>
</tr>
<tr>
<td>12</td>
<td>86.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The factors for SiO₂, Al₂O₃, etc., are referred to the shale ash as 100 percent.*
### TABLE V

**Factors Relating to the Utilization of Shales as Cement Material**

<table>
<thead>
<tr>
<th>No.</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Percent K₂O in Raw Mix</th>
<th>Lbs. K₂O per bbl. Cement, 66.6% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>106</td>
<td>2.65</td>
<td></td>
<td>0.56</td>
<td>2.15</td>
</tr>
<tr>
<td>107</td>
<td>2.58</td>
<td></td>
<td>0.55</td>
<td>2.15</td>
</tr>
<tr>
<td>114</td>
<td>3.15</td>
<td></td>
<td>0.73</td>
<td>2.93</td>
</tr>
<tr>
<td>115</td>
<td>2.87</td>
<td></td>
<td>0.57</td>
<td>2.20</td>
</tr>
<tr>
<td>116</td>
<td>2.75</td>
<td></td>
<td>0.99</td>
<td>3.72</td>
</tr>
<tr>
<td>6</td>
<td>3.02</td>
<td></td>
<td>1.36</td>
<td>5.46</td>
</tr>
<tr>
<td>7</td>
<td>3.37</td>
<td></td>
<td>1.32</td>
<td>5.30</td>
</tr>
<tr>
<td>10</td>
<td>3.29</td>
<td></td>
<td>1.40</td>
<td>5.28</td>
</tr>
<tr>
<td>11</td>
<td>3.70</td>
<td></td>
<td>1.30</td>
<td>4.50</td>
</tr>
</tbody>
</table>
Michallis Formula

\[ \frac{\text{Percent } \text{CaO}}{\text{Percent } \text{SiO}_2 + \text{Percent } \text{Al}_2\text{O}_3 + \text{Percent } \text{Fe}_2\text{O}_3} = 2 \]

We have assumed that a pure limestone is to be used and that the only loss in burning is due to loss of CO₂. The question as to whether or not loss of water or other volatile matter in the shale should be taken into account seems to be taken care of by the fact that our analyses were made on ignited material. Since the ratio of calcium carbonate to calcium oxide is 1.78, the amount of limestone needed in the raw mix per one hundred parts of shale would be equal to 3.56 times the sum of the percentage of silica, ferric oxide and alumina, or

\[
\text{Percent } \text{K}_2\text{O} = \frac{100 \times \text{Percent } \text{K}_2\text{O in Shale}}{100 + 3.56 \times \left[ \text{Percent } (\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3) \right]}
\]

Assuming that no potash was lost in the burning, the percent of potash in the final cement would be:

\[
\text{Percent } \text{K}_2\text{O in cement} = \frac{100 \times \text{Percent } \text{K}_2\text{O in Shale}}{100 + 2 \times \left[ \text{Percent } (\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3) \right]}
\]

Assuming 66.6 percent recovery, the yield of potash per 380 barrels (400 pounds) of cement would be:

\[
\text{Lbs. } \text{K}_2\text{O per barrel of cement} = \frac{100 \times \text{Percent } \text{K}_2\text{O in Shale}}{100 + 2 \times \left[ \text{Percent } (\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3) \right]} \times 666 \times 2
\]

The assumption that 66.6 percent of the total potash in the raw mix is recoverable is based on the experience of the Riverside
Portland Cement Company (14).

Samples Nos. 106, 107 and 115 are from Johnson County and are the ones which Mr. Westhafer found to have value for their oil content. The ash factors on these shales are very low and their potash content is only normal:

<table>
<thead>
<tr>
<th>No.</th>
<th>%Ash</th>
<th>%K₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>106</td>
<td>38.5</td>
<td>2.4</td>
</tr>
<tr>
<td>107</td>
<td>43.8</td>
<td>2.4</td>
</tr>
<tr>
<td>115</td>
<td>39.0</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Since the potash content is such as to give the residues from these shales no special interest, it is not likely that they will be used for cement making, except under very special circumstances. The composition of the ash would seem to permit its use for cement manufacture. If these shales were to be distilled for oil, it is conceivable that the retort residue might be disposed of to good advantage by making cement of it, especially since there would be no quarrying cost and the carbonaceous matter remaining in it might become a fuel factor in burning.

R. W. Lesley (55) has recently been granted a patent on a process for the utilization of oil shales in the manufacture of cement which embodies essentially the same procedure outlined above. He has also found that oil shale residues may be used for cement material. He proposes to distill oil shale in retorts heated by the exit gases from the cement kiln, and to use the fixed gases coming from the shale for heating the kiln.
Sample No. 114 from Moultrie County is another highly carbonaceous shale from which Mr. Westhafer has obtained a tar yield of 13.7 gallons per ton. From its analysis, the residue could be used for cement. However, it is to be regarded as a poorer prospect than 106, 107 and 115, since its potash content (3.1%) is not materially higher, while its oil factor is very much lower.

Sample No. 116 is from Logan County and was taken from a slag dump at a coal mine at Lincoln. It was collected for Mr. Westhafer by a student, Ralph Gale. Both the origin and reliability of this sample is doubtful. However, its relatively high potash content (3.9%) and its occurrence at some distance from other samples makes it worth while to report.

This sample with a silica-alumina ratio of 2.75, would give a raw mix containing almost one percent of potash and would yield, according to our method of estimating, 3.72 pounds of potash per barrel of cement.

Samples Nos. 1 and 2 are from an eight foot section of greenish gray shale lying above the uppermost part of the black shale on Caney Creek. These samples were received after our attention had been diverted from the cement making possibilities of the shales, and since they were of no special interest for their potash content, they were not studied further.

Samples Nos. 5, 8 and 9 were received late in the course of this investigation and have not been studied with special reference to their cement making qualities.
Sample No. 5 consisted of only a few ounces which was sent down from Dixon, Illinois, with very little description of its source. It is said to be from a deposit that has been used for cement making, but this statement has not been verified. It is a green sandy friable shale entirely different in character from the black shales which we have received from the southern part of the state. Its potash factor (5.8%) is the highest that we have found in any shale.

We had made arrangements to be furnished with other samples from the Dixon quadrangle, but the material did not arrive until a late date and when it did come no key was furnished which would give us the source of the samples. We are unable, therefore, to draw any conclusions as to the value or general distribution of this type of high potash shale.

Sample No. 8 was taken from an outcrop of black shale at State Pond, about 2 miles north-west of Jonesboro. The outcrop is on State land. It is of the same formation as the outcrop on Caney Creek, which is to be considered fully in our discussion of samples Nos. 6 and 7. The potash factor (5.5%) and its general appearance make it seem very probably that it is essentially the same as the material outcropping on Caney Creek and what is said of the latter material may quite safely be applied to sample No. 8.

Sample No. 9 consisted of about 40 pounds of black shale taken from a deposit about one-half mile south-west of Mountain Glenn. It also seems to be the same formation as that out-crop-
ing at State Pond and on Caney Creek. All that we have done with this shale has been to determine its potash factor. This was found to be 5.6.

The discovery of the outcrops represented by Samples Nos. 8 and 9 has been of some interest to us, since it shows that material of this kind is more widely distributed than we at first supposed.

Samples Nos. 3, 4, 6, 7, 10, 11 and 13 are all from various horizons of the black shale on Caney Creek. Samples Nos. 6 and 7 cover practically the whole thickness of the deposit. They are best that have been obtained and their composition has been better and more completely determined. We will, therefore, discuss this deposit as it is represented by these two samples.

Samples Nos. 6 and 7 of about 90 pounds each were taken by T. E. Savage and represent twenty-two feet of the deposit on Caney Creek in Union County. Sample No. 6 is from the lower eight feet and sample No. 7 is from the twelve-foot section next above sample No. 6. The outcrop is fairly well exposed and material could be obtained in quantity from it without excessively high quarrying cost. It is also within thirty rods of the railroad.

The shale itself is dark brown to black in color with thin laminations which are so uniform as to make the material appear almost massive. Microscopic examination of thin sections has proved the material to be very fine grained. Small vuggs of pyrite are found scattered through the shale, otherwise it is
quite homogeneous.

Grinding of the material is fairly easily accomplished. By passing samples of buck wheat size through a Sturtevant roll mill and then grinding in a ball mill for two hours, a fineness of 200 mesh has been obtained.

The moisture content which is a pertinent factor when considering the grinding of such material on a commercial scale, is certainly low enough so as not to cause difficulty. As we have received them, the samples have contained 0.6 percent of water. It is not likely that the fresh unweathered rock would run so high in moisture as to cause difficulty in grinding operations, as they are ordinarily carried out in cement manufacture.

The following analyses give the factors which we have obtained, calculated to the basis of the raw shale as 100 percent. Note that our analyses were made using the ash as a sample and that we have calculated the percentages of the mineral constituents as they occurred in the original rock by using the ash factor. It is not to be inferred that the sulphur occurred as sulphate in the raw shale, but since part of it was converted into sulphate on ignition and therefore not lost in that operation, it is included in the analysis.
The sulphate determination included here was made by boiling a one gram sample of the ash with 200 cc. of 5% hydrochloric acid for thirty minutes, then filtering and precipitating with barium chloride.

The following reasons are offered for the failure of these analyses to total up to 100 percent:

We suspected that in the ignition some combined water still remained with the sample. This had been partially verified by igniting a one gram sample of the ash very strongly over a blast lamp. The ash from sample No. 6 showed a loss of 1.1%. It cannot be said definitely that part of this loss might not have been due to loss of SO₃, since only a qualitative test was used to determine its presence in the strongly ignited residue. There
is the further possibility that some of the carbon might have been included in the shale particles and thus escaped oxidation even after a thorough ignition.

A qualitative test for manganese was made by fusing about one gram of the shale with sodium carbonate and then treating with nitric acid and lead peroxide. A faint pink coloration which would indicate only a trace of manganese was observed.

Titanium was tested for both by fusion with sodium peroxide and subsequent acidification with sulphuric acid and by fusion with potassium pyrosulphate followed by treatment with a little sulphuric acid and hydrogen peroxide. In both cases a slight yellow color indicating a trace of titanium was obtained.

The chemical composition of samples Nos. 6 and 7 is such as to give them silica-alumina ratios of 3.02 and 3.37, respectively. These ratios are well within the allowable limits which according to Bleininger are 2.5 and 3.5.

The iron and alkali content is such as to give a low burning mixture.

Magnesia is probably low enough so as not to be objectionable.

The sulphur content of these shales is high and might possibly interfere seriously in an attempt to make cement of them. The sulphur factor does not occur in the analyses given above, since it is almost entirely in the pyritic form and would all be either lost or converted into sulphate on ignition. Analyses for total sulphur were made on both samples by the Parr peroxide
bomb method, as it is applied to coal. One-half gram samples of shale were mixed with a measure of sodium peroxide, one-half gram of benzoic acid and one gram of potassium chlorate and fused in the ordinary way in a peroxide bomb. The fusion was dissolved in 300 cc. of water, acidified with dilute HCl and filtered from a slightly insoluble residue. The sulphur was precipitated from this solution by barium chloride without removing the iron or silica. The analyses obtained were:

<table>
<thead>
<tr>
<th></th>
<th>No. 6</th>
<th>No. 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent Sulphur</td>
<td>2.4</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Bleininger points out that sulphur in cement is objectionable and should not be higher than three percent in the finished product. When one considers the sulphur that would be introduced from the fuel and also that usually added as gypsum, there is a possibility that the sulphur content of a cement made from these shales would be high. With regard to sulphur in cement, Meade says that pyrite in the coal is not objectionable, since it is not taken up by the cement.

The inert mineral content which is a measure of the amount of material too coarse to react readily with the limestone in the cement burning process was determined for samples Nos. 6 and 7 by the method outlined by Bleininger.

One gram of raw shale ground to 100 mesh was mixed thoroughly with 8 grams of calcium carbonate by grinding in an agate mortar, and was then heated in a platinum crucible for one hour over a Meker burner. The cintered mass was disintegrated with
water and treated with dilute hydrochloric acid. In a short time practically everything had gone into solution. The solution was decanted through a filter and the residue washed successively with water, 10 percent sodium carbonate solution, and dilute hydrochloric acid, and was then transferred to the filter, washed with water, ignited and weighed.

The factors obtained were:

<table>
<thead>
<tr>
<th></th>
<th>No. 6</th>
<th>No. 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent residue</td>
<td>0.63</td>
<td>0.75</td>
</tr>
</tbody>
</table>

The high content of these shales is the feature which makes them of special interest. We have called attention in our review of the literature to the fact that the manufacture of cement affords one of the best methods for recovering potassium from shales such as the ones under consideration.

The following figures show the advantage which this material would have over material now being used. The figures for existing conditions are taken from the work of Ross and others (13), who studied the raw mix and finished product for over one hundred cement companies in the United States.

<table>
<thead>
<tr>
<th></th>
<th>Av. American Plants</th>
<th>Calculated Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No. 6</td>
<td>No. 7</td>
</tr>
<tr>
<td>Percent $K_2O$ in raw mix</td>
<td>0.90</td>
<td>1.36</td>
</tr>
<tr>
<td>Lbs. $K_2O$ per barrel, 66.6 percent recovery</td>
<td>2.73</td>
<td>5.46</td>
</tr>
</tbody>
</table>

These figures show that if sample No. 6 were to be used for cement making, there would be a possibility of recovering exactly
twice as much potash as could now be recovered by the average cement plant. Taking the price of potash as 15 cents a pound, which is about what fertilizer salts may be obtained for at the present time, the value of the potash recoverable from sample No. 6 would amount to 83 cents per barrel of cement.
4. Constitution of Southern Illinois shales

The shale from Southern Illinois (Union County, on Caney Creek) has a potash content of about 5 percent in the raw state. A product containing 5.6 percent $K_2O$ may be obtained by igniting the shale. The shale from Dixon (Lee County, Northern Illinois) contains 5.8 percent $K_2O$, but little concentration can be effected by ignition. Both of these shales compare favorably with the greensands of the East as far as potash content is concerned. Ashley, Hicks and others (23) have found the potash content of greensand to be between 5 and 7 percent. We have noted in our review of the literature that greensand is about to be worked for its potash content by methods other than those involving the manufacture of cement. The following data relating to the constitution of these shales has been obtained as a preliminary step in that part of our work, which has been directed toward the utilization of Illinois shales in ways aside from cement making.

In taking up this phase of the work, we will first describe our methods for obtaining the data, and then follow this with a tabulation of the results (Table VI) and a discussion of their meaning.

A. Experimental Procedure

Microscopic examinations were made on thin sections taken from three specimens of the Southern Illinois shale. L. E. Kennedy and T. T. Quirke of the Geology Department kindly examined these sections for us. Mr. Quirke also examined some of the Dixon shale in a powdered condition under the binocular microscope.
TABLE VI

Constitution of Illinois Shales

<table>
<thead>
<tr>
<th></th>
<th>Southern Illinois</th>
<th>Dixon Shale (Northern Illinois)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microscopic</td>
<td>Fine grained</td>
<td>Coarse grained</td>
</tr>
<tr>
<td>Examination</td>
<td>Finely divided pyrite</td>
<td>Almost a sandstone</td>
</tr>
<tr>
<td></td>
<td>No typical potassium mineral in quantity</td>
<td>Considerable quartz</td>
</tr>
<tr>
<td></td>
<td></td>
<td>No typical potassium mineral</td>
</tr>
<tr>
<td>Gravity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lighter</td>
<td>(Water 5.84)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(CH₂I₂ 6.10)</td>
<td></td>
</tr>
<tr>
<td>Heavier</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rational Analysis</td>
<td>54.50 Percent</td>
<td></td>
</tr>
<tr>
<td>Clay</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feldspar</td>
<td>7.50 &quot;</td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
<td>33.00 &quot;</td>
<td></td>
</tr>
<tr>
<td>Potash Soluble in Conc. H₂SO₄</td>
<td>3.10 Percent</td>
<td>0.90 Percent</td>
</tr>
<tr>
<td>Nitrogen as NH₃</td>
<td>0.22 Percent</td>
<td>None</td>
</tr>
<tr>
<td>Pyritic Sulphur</td>
<td>1.40 Percent</td>
<td></td>
</tr>
<tr>
<td>Sulphate Sulphur</td>
<td>0.20 Percent</td>
<td></td>
</tr>
<tr>
<td>Free Oil</td>
<td>3.40 Gallons per ton*</td>
<td>None</td>
</tr>
<tr>
<td>Oil on Distillation</td>
<td>1.20 Gallons per ton</td>
<td>None</td>
</tr>
</tbody>
</table>

* An estimate, calculated on the assumption that the oil would have a specific gravity of 0.9
Attempts at a gravity separation have been made using both methylene iodide and water.

The method of using methylene iodide was to suspend some of the ground material in this reagent and then reduce the gravity of the liquid by adding benzene. A special sample was prepared for this test. It was ground by hand in a porcelain mortar and at frequent intervals the finer particles were removed by by the use of a 100 mesh sieve. The grinding and screening was continued, however, until the whole sample had been passed through the sieve. This procedure was taken in order to get a finely divided product which would be as free as possible from very fine dust. The presence of very much fine dust in the sample would make a suspension which would be colloidal in nature, and little separation would take place even if constituents of different gravity were present. By adjusting the gravity of the solution, we were finally able to cause the sample to remain suspended throughout the whole depth of the column of methylene iodide. The only visible indication that any separation was taking place, was the appearance of a small amount of pyrite at the bottom. However, after the suspension had stood for over a month a small layer was found to have gathered at the top and it was separated and analyzed.

A gravity test using water was carried out by allowing 100 grams of finely ground shale ash to settle through a three foot column of water contained in a 2-1/4 inch glass tube. The ash was suspended in three hundred cc. of water and carefully poured into the top of the tube. About two hours was required for it
to settle into a cake about three inches thick at the bottom. The arrangement at the bottom of the tube was such that the water could be drawn off from above the cake and the cake removed without disturbing any layers that might have been formed in the settling process. The cake was, however, given several days in which to become more compact. After the cake had been removed, it was dried and samples were taken from the top and bottom portions and analyzed for potash.

Shale No. 6 from Southern Illinois has been analyzed by the method of rational analysis. This analysis is supposed to show the relative amount of clay substance, free silica and feldspar in a clay or shale. The theory of the rational analysis is that hot concentrated sulphuric acid will dissolve the bases in the clay substance and leave the silica that is combined with them in colloidal form. Sodium carbonate solution will dissolve this silica, but will not attack the free quartz or feldspar. The residue left after treatment with sulphuric acid and sodium carbonate is, therefore, the free quartz and feldspar. Alumina is then determined in the quartz-feldspar residue and the feldspar is calculated from the alumina factor by multiplying by 5.48. A detailed description of the method will be found in Mellor's Treatise on Quantitative Analysis, page 658.

The supposition that the clay substance of a clay or shale is completely decomposed by sulphuric acid while the feldspar is not attacked, has led us to use this reagent to determine in which of these two forms the potash in these shales is held. Our pro-
procedure has been to boil one gram of shale with 25 cc. of sulphuric acid until about half of the acid has been driven off, then to cool down, dilute with water, filter, wash, ignite gently in a platinum crucible and analyze the residue for total potash by the method of J. Lawrence Smith. The residue could always be quite completely removed from the crucible, but the decomposition with ammonium chloride and calcium carbonate was carried out in the same crucible so that any small particles that might have been left in it would not be lost in the analysis. The difference between the potash found in the residue and the total potash content of the shale would be a measure of the potash in the clay substance. Our reason for analyzing the residue rather than the solution was that the solution contained large amounts of sulphuric acid and soluble bases which would make its analysis difficult.

Nitrogen and free oil determinations have been made on the Southern Illinois shale. From the nature of the Dixon shale, there would obviously be no need to look for these constituents in it. Nitrogen was determined by the Kjeldahl method, using potassium sulphate, copper sulphate and sulphuric acid.

Pyritic sulphur has been determined for the southern Illinois shale by the method worked out in this laboratory by A. R. Powell (61) for pyrite in coal. The determination is made by treating a one gram sample with 80 cc. of nitric acid of a specific gravity of 1.17 and allowing to stand for four days. The solution is then filtered and the sulphate precipitated with barium chloride.

Sulphate sulphur was determined by boiling one gram of the shale with 300 cc. of 5 percent hydrochloric acid for thirty min-
utes, then filtering and precipitating with barium chloride.

In an attempt to show whether the potash in the southern Illinois shale might be held in some sort of an adsorbed condition, a ten gram sample was subjected to the leaching action of hot water for a long period of time. The extraction was carried out in a Soxhlet apparatus and a blank determination was run to check up on the potassium that would be dissolved from the glass. The solutions were analyzed after 48, 168 and 388 hours. Since the data cannot be conveniently included in Table VI, it will be given here.

Potash Extracted by Water

<table>
<thead>
<tr>
<th>Time</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>48 hours</td>
<td>0.087</td>
</tr>
<tr>
<td>48-168 hours</td>
<td>0.073</td>
</tr>
<tr>
<td>168-388 hours</td>
<td>0.023</td>
</tr>
</tbody>
</table>

Free oil was estimated by extracting a ten gram sample of finely ground material with benzene in a Soxhlet for three hours and evaporating off the benzene on a water bath until about 10 cc. remained. The flask which had been previously weighed was then put in an oven at 105° and heated until it came to fairly constant weight. The quantity of oil obtainable in this way was not
sufficient to permit of an examination as to its nature. It appeared, however, to be a petroleum oil of good quality. It was not possible to get either the volume or the specific gravity of the oil. We have estimated the yield in gallons per ton on the assumption that its specific gravity would be 0.9.

A destructive distillation of the black shale was also made. 500 grams of finely ground shale was placed in a one-liter Pyrex distilling flask connected with an air condenser. The flask was surrounded by asbestos paper and heated by means of a one inch Meker burner. The arrangement was such that at the end of the distillation a thermometer extending down into the neck of the flask a little below the side tube showed a temperature of 350°. The flask was heated gently at first, then more strongly until at the end of four hours, when no more distillate was coming off, the temperature of the shale must have been about 450°. Some gas came off during the first part of the distillation. The distillate consisted of 5 cc. of a dark brown oil and 16 cc. of water containing some ammonia. The oil was redistilled from a small distilling flask. Its boiling point ranged from 80 to 360°. The larger part seemed to boil above 160°.

B. Discussion and Conclusions.

The microscopic examination of the shale was unsatisfactory because of the very fine grain of the southern Illinois shale and because of the fact that the friable nature of the Dixon shale would not permit the preparation of a thin section.
The southern Illinois shale probably contains small amounts of muscovite $\text{KH}_2\text{Al}_3(\text{SiO}_4)_3$ and occasional grains of feldspar, but not enough of both to account for all of the potash contained in the rock.

All that could be determined by the microscopic examination of the Dixon shale was that it is of an entirely different type than that from southern Illinois.

Specific gravity tests which were conducted only on the southern Illinois shale show that there is a slight tendency for the potash to become concentrated in the lighter material. The small difference in specific gravity of the constituents of this shale and its very fine grain size preclude the separation by gravity of any of its components except pyrite.

The rational analysis has been made simply because it is the only chemical method that has been worked out for the estimation of "clay substance" feldspar and quartz in a clay or shale. Mellor states that the procedure may give results of quite wide variation in the hands of different workers even where directions are followed with greatest care. Although the factors obtained seem reasonable, we are not inclined to put a great amount of faith in them.

The solvent action of concentrated sulphuric acid on the potash of the two shales shows a marked difference in their constitution. Sixty-two percent of the total potash content of the southern Illinois shale is dissolved by this reagent, while only 15 percent of that contained in the Dixon shale is
removed under the same conditions. This difference in the solubility of the potash in these shales is in agreement with a number of other solubility tests which we have made, and which are to be taken up later.

Considering the theory on which the rational analysis is based, it would seem that the potash in the southern Illinois shale is largely contained in the "clay substance" or decomposed part of the rock. At any rate, the mineral which is holding the sulphuric acid soluble part of the potash must be secondary in nature. The number of such insoluble secondary potassium minerals is very limited. Glauconite or greensand is the only common one occurring in the United States.

On first thought, there seems no possibility that material of the nature of greensand should occur in these shales, since greensand, as it is known in the East, is formed by the action of ferric hydroxide with soluble silica and potassium in the presence of forams. The following theory of the formation of greensand is quoted from Murray and Renard by Wm. B. Clarke (63):

"The organic matter transforms the iron into sulphide which may be oxidized to hydrate, sulphur being at the same time liberated. This sulphur would oxidize to sulphuric acid, which would decompose clay, setting free colloidal silica, aluminum being removed in solution. Thus, we have colloidal silica and hydrated iron in a state most suitable for their combination. The potash which is necessary to complete the composition of glauconite may be derived from the decomposed fragments of crystalline rocks like orthoclase or white mica."

Although the soundness of a theory involving oxidations and reductions under conditions such as have been indicated may be
somewhat doubtful, the statement serves, nevertheless, to indicate that the materials and conditions which must exist where glauconite is to be formed are iron bearing material, organic matter, clay and potassium bearing rock. There seems a good probability that all of these conditions were fulfilled when the southern Illinois shale was first laid down. In the shale, as it occurs at the present time, the ratio of iron to the potassium is smaller than that usually found in greensand. When the iron combined as pyrite is deducted from the total iron, there remains 3.3 percent for the 3.1 percent of potash which is in the more easily soluble form.

Bayley in his "Descriptive Mineralogy" indicates that this ratio in greensand will be about 10-19 of iron to 7-10 of potash. However, in view of the very indefinite constitution of greensand itself, there seems to be no very good reason why the sulphuric acid soluble potassium material in the southern Illinois shales might not be considered as of the greensand or glauconite type.

From its lack of solubility in acid, the potassium in the Dixon shale would seem to be almost altogether in the form of undecomposed rock of the feldspar type. As a matter of fact, the microscopic examination of the Dixon shale shows that it had undergone very little decomposition, and for that reason should not be regarded as a shale.

Nitrogen was known to be present in the southern Illinois shale, because of the fact that some ammonia was recovered when the shale was destructively distilled. The analytical factor was obtained in order to find out to what extent it was present.
The nitrogen content was found to be only 0.32 percent, calculated as NH₃. It adds little, therefore, to the value of the shale.

Free oil, although hardly to be expected in material of this type, was found to be present in appreciable amounts. The amount of oil present is not large enough for it to add any value to the shale. The discovery of its presence in the shale has been of considerable interest to us, however, since it may possibly be the explanation for the fact that the potash has not leached from the decomposed part of the shale as it has in the ordinary clays and shales.

The oil obtainable on destructive distillation of the shale is of little interest. A determination was made mainly for the purpose of adding a little more to the study of the bituminous part of the shale. It is interesting to note that our value of 1.2 gallons per ton, as well as Mr. Westhafer's (1.7 gallons per ton) is quite a little less than that which we have been able to extract.

5. The action of liquid reagents on southern Illinois and Dixon shales

Our work on the constitution of the southern Illinois shale has shown that it is not of the ordinary type of potassium bearing rock. It has also indicated that the shale might be expected to yield its potash by extraction methods. In order to determine to what extent the potassium can be dissolved from this shale by common reagents, a number of them have been tried out on small samples. Their effectiveness has been determined by analyzing the solutions quantitatively for potassium, using perchloric acid. Since the data that had been obtained on the Dixon shale was not sufficient to warrant our dropping the con-
sideration of its extraction by such methods, some of these tests were also applied to feldspar.

The solutions obtained in these extractions contained sodium, calcium or magnesium chloride; aluminium and iron salts; sulphates; and occasionally silica. According to Mellor's Treatise on Quantitative Analysis, page 237, sulphates, and sodium, calcium and magnesium chlorides do not interfere with the separation of potassium by the perchlorate method. We have tested out iron and aluminium salts and find their perchlorates very soluble. Silica, if present in the solution, would interfere and has therefore been removed by dehydration. Aside from the removal of the silica and of the sulphates when present in large amounts by means of barium chloride, we have simply taken the solutions obtained in leaching the shales and evaporated them to small volume in porcelain casseroles, then filtered them into small evaporating dishes and precipitated the potassium by evaporating with 20 percent perchloric acid. The perchlorate precipitate was washed with 95 percent alcohol and weighed on a Gooch crucible after drying at 130°. Only one determination was made, but in practically every case, there are related tests which check the accuracy of the analysis.

Two tests which have been carried out on southern Illinois and Dixon shale and on feldspar, and one other which has been applied to the shales only, will be taken up together for purposes of comparison. These tests were as follows:
(a) Five grams of finely powdered rock was treated with 1 cc. of concentrated sulphuric acid and heated gently in a platinum crucible until the excess of acid had been fumed off. In the case of the southern Illinois shale the ash was used. The residue was then disintegrated with hot water and washed until a filtrate of 300 cc. had been obtained. The solution was analyzed as indicated above.

(b) Five grams of rock was placed in a Carius bomb tube with 20 cc. of concentrated hydrochloric acid. The bomb was sealed and heated in an electric tube furnace at 200° for 10 hours. The bomb was then cooled in the furnace, removed, opened and its contents rinsed out into a casserole. It was evaporated just to dryness in the casserole and then taken up with a little water and a few drops of hydrochloric acid and filtered into a small evaporating dish. The analysis was then completed in the ordinary way.

(c) Five grams of rock were boiled with 25 cc. of concentrated hydrochloric acid for one hour. The analysis was then carried out as in (b). In the following tabulation, the percent of potash extracted as referred to the weight of the sample is given.

<table>
<thead>
<tr>
<th>Potash Dissolved by Acids</th>
<th>So. Ill. Shale</th>
<th>Dixon Shale</th>
<th>Feldspar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. H₂SO₄</td>
<td>3.1%</td>
<td>.06%</td>
<td>.35%</td>
</tr>
<tr>
<td>Conc. HCl at 200°</td>
<td>3.8%</td>
<td>1.13%</td>
<td>.57%</td>
</tr>
<tr>
<td>Boiling Conc. HCl</td>
<td>3.1%</td>
<td>.83%</td>
<td></td>
</tr>
</tbody>
</table>
These data show that in the case of the southern Illinois shale that the limit of extraction with acid under conditions that could be maintained in a commercial process is about 3.1 percent. K₂O. Even such vigorous treatment as that of hydrochloric acid at 200°C fails to increase very materially this amount of extraction. The data on the Dixon shale supports further our contention that it is entirely different and much more stable than that from southern Illinois.

(d) Effect of Acid Concentration.

In order to determine the amount of potassium that could be extracted from the southern Illinois shale by water and by lower concentrations of acid, a series of determinations was made using water and six different concentrations of hydrochloric acid. In this test ignited shale was used. Hydrochloric acid was used rather than sulphuric, since the resulting solutions were more easily analyzed and the action of either acid would probably be the same except at high concentrations were the higher temperature attainable with sulphuric acid would become a factor. The determinations were carried out by boiling 2 gram samples with 100 cc. of acid for 3 hours. The solutions were analyzed by the methods already described.

| Potash Dissolved by Water and by Hydrochloric Acid at Different Concentrations |
|---------------------------------|------------------|
| K₂O in percent. of the weight of the sample |
| Water                           | .25              |
| 2.2 percent. HCl                | 1.30             |

(continued above)
4.4 percent. HCl 1.60
6.6 \text{ "} \text{ "} 2.30
8.8 \text{ "} \text{ "} 2.45
11.0 \text{ "} \text{ "} 2.85
37.0 \text{ "} \text{ "} \text{ Conc.} 3.10

The conclusion to be drawn from this series of experiments is that although more than a slightly acid solution is required to effect the solution of much of the potash, the limit of acid solubility which seems to be 3.1% is approached when acid considerably weaker than concentrated hydrochloric is used. At any rate the amount of potassium brought into solution under the most favorable conditions is not large enough when the necessary leaching and evaporating operations are considered, to warrant our continuing much further along this line of attack.

(c) Efficiency of Sulphuric Acid Extraction.

In order to get an estimate of the efficiency of a process in which only the acid which actually combined with the shale would be lost, an experiment suggested by Professor Noyes was performed. One hundred grams of raw shale was treated in a distilling flask with 300 grams of sulphuric acid and the excess acid distilled off and collected. At the same time the residue in the flask was leached and the solution analyzed for soluble potash.

In carrying out this experiment the arrangement was the same as that used in the destructive distillation of the shale.
The air condenser dipped down into water in a 2-liter volumetric flask. It was not possible to drive all the acid from the shale, but the quantity that remained was determined by titrating the leached solution. The acid was estimated in the distillate by diluting that which had been collected to 2 liters and then titrating to 10 cc. portions after boiling them in order to expel sulphur dioxide. In leaching the residue about 750 cc. of hot water was used. For the estimation of the potassium and the acid, aliquots were taken from this solution after it had been diluted to 1 liter.

Action of Sulphuric Acid on Southern Illinois Shale.

<table>
<thead>
<tr>
<th>Amount of shale</th>
<th>100 grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of H₂SO₄ used</td>
<td>300 grams</td>
</tr>
<tr>
<td>K₂O extracted</td>
<td>3.0 percent</td>
</tr>
<tr>
<td>H₂SO₄ in distillate</td>
<td>15.7 grams</td>
</tr>
<tr>
<td>H₂SO₄ in residue</td>
<td>36.7 grams</td>
</tr>
<tr>
<td>H₂SO₄ lost</td>
<td>247.6 grams</td>
</tr>
</tbody>
</table>

The amount of sulphuric acid destroyed when raw shale is treated in this way is found to be almost equal to 2.5 times the weight of the shale used. It was known that this loss would be considerable, due to the fact that all of the organic matter in the shale would have to be oxidized at the expense of the sulphuric acid, but we did not anticipate that it would be so large as our results indicate.

(f) Oxidation of Pyrite.

In our review of the literature, we have discussed the
preparation of aluminium sulphate from carbonaceous shales containing pyrite, by a method which depends upon the spontaneous oxidation of the pyrite to ferrous sulphate and sulphuric acid, and the subsequent reaction of these reagents on the shale. This same procedure would seem to be directly applicable to the southern Illinois shale, but unfortunately the weathering operation could not be carried out experimentally. The question has naturally come up as to whether the oxidation of the pyrite might not be brought about by some more rapid method. To this end two experiments have been undertaken. In the first test a funnel was placed inverted in a two liter beaker and one kilo of 200 mesh shale poured around it. Air was blown into the mass through the funnel for four weeks. Before being passed into the shale, it was washed by passing through a solution made by diluting one volume of concentrated nitric acid with ten of water. We thought that in this way traces of nitric acid would be carried over with the air which might have a catalytic action in promoting the oxidation.

The second test consisted in blowing air and steam into one kilo of the shale for four hours. At the end of this operation the water which had collected in the shale was evaporated off and the residue was crushed up, sampled and dried. This product, was well as that obtained in the previous experiments, and a sample of the untreated shale was analyzed for sulphate. The analysis was carried out by boiling 2 gram samples with 200 cc. of 5 percent. hydrochloric acid, filtering and precipitating
with barium chloride.

Oxidation of Pyrite

Percent. SO\(_2\)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>SO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>.5%</td>
</tr>
<tr>
<td>Blown with air and HNO(_3)</td>
<td>.4%</td>
</tr>
<tr>
<td>Blown with air and steam</td>
<td>.55%</td>
</tr>
</tbody>
</table>

These results show that no oxidation of the pyrite takes place under this treatment.

(g) Other tests.

A number of other tests using various liquid reagents have failed to add anything to what has been given.
6. The action of solid reagents on shales.

The amount of data that has been obtained relating to the action of solid reagents on these shales is very meager. The reason that more work has not been done along this line is that the methods that have been proposed have all been for the utilization of feldspar and it has seemed that the shales should yield to less vigorous treatment.

Following up the results that have been obtained by the use of hydrochloric acid at high temperatures, we have investigated the properties of magnesium chloride.

When hydrated magnesium chloride is heated, it hydrolizes slowly with the evolution of HCl. A preliminary test has shown that HCl is still being evolved when the salt is brought slowly to a low red heat. It would be of theoretical interest at least to know whether the shale would be attacked by the hydrochloric acid as it is evolved at these elevated temperatures. There is the further possibility that partially dehydrated magnesium chloride might be used to replace the ammonium chloride used in the J. Lawrence Smith method for analysing silicate rocks. Two experiments have been performed to test out these theories. At the time when these ideas occurred to us, we were working on the Dixon shale and consequently it was used in the tests. The results would have been of greater interest if the southern Illinois shale had been used.

The first test was made by partially dehydrating three grams of MgCl₂. 6H₂O and then mixing it by grinding with five
grams of shale. The mixture was heated in a shallow porcelain dish, heated gently at first and then more vigorously until finally the bottom of the dish was at a low red heat. At this time a small amount of HCl was still being evolved. The heating was continued for about a half hour and then the product was cooled and leached with 200 cc. of hot water. The solution was analyzed by the perchlorate method.

To determine the action of magnesium chloride in the presence of calcium carbonate one gram of partially dehydrated magnesium chloride was substituted for the ammonium chloride and the determination carried out exactly as by the J. Lawrence Smith method. The reason for partially dehydrating the magnesium chloride used in these tests was that it was rather wet and could not be easily mixed with the other ingredients. The following data were obtained:

**Action of MgCl₂ on Dixon Shale**

<table>
<thead>
<tr>
<th>% K₂O Extracted</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>MgCl₂</td>
<td>1.56</td>
</tr>
<tr>
<td>MgCl₂ &amp; CaCO₃</td>
<td>1.13</td>
</tr>
</tbody>
</table>

From these results it is obvious that potash could not be extracted commercially from the Dixon shale by means of these reagents. It is of theoretical interest to note that the amount of potash made soluble by MgCl₂ and CaCO₃ is the same as has been obtained by the action of hydrochloric acid at 200o.

The effectiveness of the extraction process patented by Cushman and Coggeshall (32) which has been taken up in our
review of the literature has been tried out on a 100 gram sample of ash from the southern Illinois shale.

For this purpose, 100 grams of ash was mixed by grinding in a mortar with 20 grams of salt and 20 grams of lime. By sprinkling the powdered material with a solution containing 20 grams of calcium chloride and shaking, the mixture was formed into pellets similar to those obtained by the authors of the patent. These pellets, along with a small amount of fine material which could not be gathered up, were heated on a roasting dish in a muffle for two hours. The temperature was maintained at a low red heat. After heating, the pellets were crushed up and the powder leached with 750 cc. of hot water. The solution was made up to 1 liter and 10 cc. portions taken and analyzed by the perchlorate method.

Potash dissolved 2.4 Percent.

We see no reason why this shale ash should be less effectively extracted than feldspar by this method. However, the results of this single test indicate that only about 43 percent of this total is made soluble, whereas the authors of the patent claim to have obtained 55 percent extraction using feldspar. Although a more careful study of the conditions might make it possible to obtain an extraction of 55 percent, it is not probable that the method could be made to do much better. In that case, it would have little interest from a commercial standpoint.
7. Action of lime under steam pressure.

The action which lime under steam pressure would have on these shales has been studied by way of following up other work which has been done in this laboratory on the reaction of this reagent on feldspar.

In our review of the literature we have taken up the previous work of Ross and Charlton. Although the results obtained by Roman (43) in this laboratory indicate that only 35 percent of the potash in a feldspar can be dissolved by lime at moderate pressures, Ross (44) has found that as high as 85 percent of the total may be taken out in this way. Charlton (46) has used lime to good advantage on green sand.

In our work on the action of lime, we have been most interested in determining whether or not the southern Illinois shale might be more easily attached than feldspar.

In all, five determinations were made. Baker's pure lime from marble was used and was prepared for use in the tests by slacking with enough water to make a fairly thin paste. In the three cases where on gram samples were used, the whole sample was leached after treatment with 200 cc. of hot water, and the solution analyzed for potash using chlorplatinic acid. In case of the determinations where a larger amount of material was treated, a proportionately larger amount of water was used in leaching and aliquot parts of the solution were analyzed in duplicate. The heating pressure was carried out in an autoclave.
of about 3 liters capacity, heated by means of a Bunsen burner. The autoclave was fitted with a thermometer well and a pressure gauge. The samples were not placed in the bottom of the autoclave, but were contained in a porcelain dish supported on a wire frame above the water which filled the autoclave about one fourth full. This dish was found to be only slightly attacked.

The test at atmospheric pressure was carried out by slack-ing 500 grams of lime in 3500 cc. of water and then stirring this up with 500 grams of shale. The batch was contained in a five liter flask and a stirring device was used to bring about vigorous and continuous agitation. The mixture was kept boiling gently for eight and ten hour periods, aggregating about 48 hours in all. Water was added to replace that lost by evaporation. The washing of this 500 gram residue presented some difficulty. Our method of accomplishing it was to filter on a Buchner and then wash the cake by beating it up again with about two liters of hot water and then filtering again. The original filter cake was washed twice in this way. The reason for using 1.85 grams of lime in three of the tests was that this amount is just a little more than would be used in making cement of this shale.

**Action of Lime on Southern Illinois Shale.**

<table>
<thead>
<tr>
<th>Shale Grams</th>
<th>Lime Grams</th>
<th>Time Hours</th>
<th>Pressure Atmospheres</th>
<th>Potash Dissolved</th>
<th>Percent. Of Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>500</td>
<td>48</td>
<td>1</td>
<td>0.65</td>
<td>13.0</td>
</tr>
<tr>
<td>1</td>
<td>1.85</td>
<td>1</td>
<td>10-11</td>
<td>1.80</td>
<td>31.3</td>
</tr>
</tbody>
</table>

(continued above)
These data show that lime under steam pressure is probably not more effective in dissolving the potash than a number of reagents that we have used, and that the shale is probably not much more easily attacked than feldspar. Observations made during the test that a reaction was taking place. After about twenty-four hours heating, the mixture seemed to be getting less granular and appeared almost curdy. The analysis does not show, however, that much potash was taken into solution.

The results of the tests where steam pressure was used show that most of the potash which can be dissolved with lime is taken out in the first hour. The last test in which 3.7 times as much lime as shale was used shows that the larger proportion of lime does not increase the amount of potash dissolved.

A probable explanation for the fact that lime is not more effective in decomposing this material lies in the fact that when the lime begins to react upon a rock particle, a coating of colloidal hydrous calcium silicate forms over its surface, consequently no further reaction takes place. Microscopic examinations made by Earnest (40) indicate that the calcium silicate formed under these conditions is colloidal in nature. F. W. Clark (59) has made some observations of the action of water on feldspar which point in the same direction. He has found that water
reacts almost instantly with finely powdered feldspar and becomes alkaline in reaction, but that the reaction comes to a complete stand still very quickly. However, when such material is subjected to the combined action of water and grinding, the reaction continues and a small amount of kaolin-like material is obtained. He also explains this phenomena by saying that a coating of colloidal silicic acid is formed.

It is evident that mere agitation is not sufficient to keep this coating removed from the rock particles, since the stirring arrangement used in the test carried out at boiling temperature was certainly as efficient as one could desire, and the boiling was continued long enough to permit of a complete reaction.

A procedure that would seem to give greater promise of success than the ones that we have tried would be one in which a grinding action accompanied the action of lime and steam. The operation could probably be carried out in a rotating steel drum, provided with axile inlets for steam and a charge of steel balls or rods to effect the grinding as the drum is rotated.

The residue which would remain after the treatment of the shale in this way might be used as a binder for sand lime brick, as in the process where greensand is used. The potash material obtainable in this way would be fairly pure potassium hydroxide.

A general conclusion which may be drawn from the results of our work on the extraction of potassium from these shales by
acids, solid reagents, and lime is that it is not commercially practical because of the incomplete solution of the potash and because of the difficulty in washing out and recovering the soluble salts from the residue.
8. Plant availability of potash in shales

The results being obtained from the experiments conducted by Professor Stewart already referred to (page 28) indicated a remarkably high plant availability of the potash in the southern Illinois shale.

It has already been shown that about two-thirds of the potassium in the southern Illinois shale is, like leucite, soluble in sulphuric acid, and that the Dixon shale yields only about 16 percent of its potash by this reagent. Here, then, is afforded an opportunity for testing the availability of the sulphuric acid soluble potash for plant use. The work of a number of investigators has shown that plants can get potassium from relatively insoluble minerals. Mr. DeTurk (52) has reviewed the literature and has offered the results of his own work which shows that leucite is one of these insoluble minerals which yields its potash readily to plants.

It has seemed of interest, therefore, to try to determine whether or not the sulphuric acid soluble potash in the shales was a measure of the availability of this element in plant growth. At the same time, it would be interesting to determine whether or not the bituminous part of the shale had any part in stimulating plant growth, and also to verify the results obtainable with the southern Illinois shales from different outcrops. With the assistance of Professor Stewart, who has kindly granted us the use of materials and also of space in the Agronomy Greenhouse, we have obtained some interesting qualitative results bearing on
these points.

The relative plant availability of the potash in the following material has been determined.

1. Kainite
2. Shale extracted with sulphuric acid
3. Potassium carbonate absorbed in clay
4. Southern shale ignited
5. Shale from Caney Creek deposit
6. Shale from State Pond deposit
7. Dixon shale

In the preparation of these materials for use in the tests, the raw shales were simply ground to 100 mesh. The ignited material was obtained by burning the carbonaceous matter from 100 mesh raw shale at a low red heat. The extraction of the southern Illinois shale with sulphuric acid presented some difficulty, since it was very difficult to wash the residue free from sulphuric acid. However, a fairly satisfactory product was finally obtained. Its acidity was determined by shaking a ten gram sample with hot water, diluting to 500 cc. and titrating portions of the supernatant liquid after the precipitate had quite completely settled. The acid in one gram of the shale required .4 cc. of 3/10N KOH which is equivalent to .0039 grams of sulphuric acid. This amount is equivalent to .0040 grams of limestone. It has been calculated that for the amount of material used in one of the pots, that .32 grams of limestone would be required for its neutralization. Since the amount of limestone added
to the pots was 60 grams, it would not seem that the acid left in the shale should interfere.

The test in which clay and potassium carbonate was used was carried out in an attempt to verify the theory that clay might be made to absorb or adsorb potassium salts to produce a material similar in nature to the southern Illinois shales. The test has been so unsatisfactory that little discussion of our procedure is necessary.

Curry and Smith (60) and others have found that ordinary soil and especially clay takes up soluble potassium salts and makes them completely insoluble in water. We have attempted to incorporate some potassium carbonate into a Tennessee ball clay, but were unable to cause much potassium to remain with the clay or to be sure that the excess of water soluble potassium had been completely removed. A product containing 2.2 percent of potassium as against about 0.7 percent in the original clay was obtained. A determination of water soluble potash was made by washing a 2 gram sample of the final dried product with 200 cc. of hot water. The amount of water soluble potash was found to be 0.35%.

Buckwheat was used as the crop on which to try these materials, since it has proved in Professor Stewart's work to be rather sensitive to varying conditions of potash in the soil. Peat was used as the soil in which to grow the plants since it is characterized by a deficiency in potassium and has also been used by Professor Stewart.
The preparation of the pots was done under the direction of Mr. Anderson, who has assisted Professor Stewart in his work. Sixteen pots were prepared using eight different treatments in duplicate. The pots were numbered consecutively from 1 to 8. The duplicate pots were designated by the letter "A" following the number.

It was found that seven kilos of the fresh peat would be about the right amount for the four gallon jars used, so that amount was weighed out in a tin box which was large enough to permit of the thorough stirring of the peat in it. Sixty grams of lime was added in all cases. After this there was added to each pair of pots the different potassium materials in amounts equivalent to 1.34 grams of the element potassium. The limestone and potash material was very thoroughly mixed with the peat after which it was placed in the jars, wet down thoroughly and planted on March 5th, 1920. When the plants were out of the ground, they were thinned so that about twelve remained in each pot. Notations as to the appearance of the series were made on March 30th and on April 14th. Photographs of the pots were taken on April 29th.

The treatment accorded the different pots and the numbers assigned to them are given on the following page. Pots marked 1A, 2A, 3A, etc. are duplicates of those marked 1, 2, 3, etc.
Treatment of Test Pots

<table>
<thead>
<tr>
<th>Lime Grams</th>
<th>Potash Material</th>
<th>Amount Grams</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 and 1A (checks)</td>
<td>60</td>
<td>None</td>
</tr>
<tr>
<td>2 and 2A</td>
<td>60</td>
<td>Kainite</td>
</tr>
<tr>
<td>3 and 3A</td>
<td>60</td>
<td>Shale extracted with $\text{H}_2\text{SO}_4$</td>
</tr>
<tr>
<td>4 and 4A</td>
<td>60</td>
<td>Clay and $\text{K}_2\text{CO}_3$</td>
</tr>
<tr>
<td>5 and 5A</td>
<td>60</td>
<td>Ignited So. Ill.</td>
</tr>
<tr>
<td>6 and 6A</td>
<td>60</td>
<td>State Pond Shale</td>
</tr>
<tr>
<td>7 and 7A</td>
<td>60</td>
<td>Caney Creek Shale</td>
</tr>
<tr>
<td>8 and 8A</td>
<td>60</td>
<td>Dixon Shale</td>
</tr>
</tbody>
</table>

On May 30th, four weeks after planting, the plants had grown to an average height of eight inches and there was no wide variation from pot to pot. The Caney Creek, State Pond, Dixon and ignited shales were all doing about the same. They were showing a little faster growth than the checks, but were not doing so well as the kainite. The extracted material at this time was showing poorer growth than the checks.

Notations made on April 14th, six weeks after planting, show that the plants ranged in height from 20 to 32 inches. At this time, the Caney Creek and State Pond shale and the kainite pots were all showing about equal growth. The plants growing in the ignited southern Illinois shale were probably doing a little better than any of the others.

The Dixon shale at this time was doing little or no better
than the checks.

The sulphuric acid extracted material had overcome to some extent the backward growth that had been observed on May 30th, but was still a little poorer growth than the checks.

The pots were photographed on April 39th, with the pots arranged in such a way as to bring out the different facts which they are intended to substantiate.

Plate III shows all of the pots and serves to show the uniformity in growth between the duplicates. The pots in the lower photograph are the duplicates of those bearing the same number in the upper one.

Plate IV shows the relative availability of the southern Illinois shale, either raw or ignited, compared with kainite.

Plate V shows the relative merits of the southern Illinois shale as compared with that from Dixon.

Plate VI shows the relative inavailability of the potash in the Dixon shale and also that remaining in the southern Illinois shale after extraction with sulphuric acid.

The conclusions to be drawn from the results of these pot tests are:

1. The high potash shales of the type occurring in southern Illinois seem to be alike as regards the availability of their potash content.

2. Ignition of the southern Illinois shale may increase slightly the availability of its potash content.

3. The potassium in the Dixon shale is not available.
4. Sulphuric acid removes the available potash from the southern Illinois shales and makes it seem probable that it is only the acid soluble potash which is held in the decomposed rock or clay substance which is available to plants.
PLATE III

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Check</td>
<td>Kainite</td>
<td>H₂SO₄</td>
<td>K₂CO₃</td>
<td>Ignited</td>
<td>State</td>
<td>Caney</td>
<td>Dixon</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Extracted Shale</td>
<td>in Clay</td>
<td>Shale</td>
<td>Pond Shale</td>
<td>Creek Shale</td>
<td>Shale</td>
</tr>
</tbody>
</table>

COMPLETE SERIES OF TEST POTS
COMPARISON OF KAINITE AND SOUTHERN ILLINOIS SHALE
PLATE V

6 7 8
State Caney Dixon
Pond Creek

COMPARISON OF SOUTHERN ILLINOIS AND DIXON SHALE
TABLE VI

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>3</th>
<th>8</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Check</td>
<td>H₂SO₄</td>
<td>Dixon</td>
<td>Kainite</td>
<td></td>
</tr>
<tr>
<td>Extracted</td>
<td></td>
<td>Shale</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

SOUTHERN ILLINOIS SHALE EXTRACTED WITH SULPHURIC ACID COMPARED WITH DIXON SHALE
V CONCLUSIONS

1. Shales occur in at least two localities in this State which contain five percent or more of potash.

2. Shale outcropping in several places near Jonesboro in Union County which contains five percent of potash would be suitable, so far as can be determined from its chemical composition and physical character, for use in the manufacture of Portland cement.

3. By using this material in the manufacture of cement and by applying the known methods of potash recovery, a yield of 5.3 pounds of potash, representing a value of 70-80 cents, per barrel of cement could be obtained.

4. The constitution of the southern Illinois shale is complex. The shale contains free oil, bituminous matter, pyrite, undecomposed potassium bearing rock, feldspathic in character, and potassium bearing material of the nature of glauconite or greensand.

5. Shale from Dixon contains 5.8 percent of potash which is held for the most part in a more stable combination than that in the southern Illinois shale.

6. Extraction of the potassium from shale of either the southern Illinois or Dixon type is impracticable, because of the incomplete reaction of these reagents on the shale and because of the cost of leaching and recovering potash from material where it is present in such small amounts.
7. The plant availability of the potash in the southern Illinois shale is probably characteristic of all of the material of this type outcropping in that locality.

8. That part of the potassium in the southern Illinois shale which is soluble in sulphuric acid, is shown to be in a combination of the glauconite type.

9. In southern Illinois shale having a potash content of 5.0 percent in the raw condition or 5.6 percent when ignited, 62 percent of the total potash is glauconitic in character and is available as a plant food.
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VITA

The writer of this thesis was born on a farm near Waterloo, Wisconsin, December 19th, 1892. Following his primary school training in a country school, he entered high school at Columbus, Wisconsin, and graduated after a four years course in 1911. The year following graduation from high school and most of the vacation periods since were spent on a farm. He entered Lawrence College, Appleton, Wisconsin, in the fall of 1912, and after four years at that institution was graduated with the degree of Bachelor of Arts. In the fall of 1916 he took up graduate work in the Department of Chemistry at the University of Illinois, and has continued in that work until the present time. He received the degree of Master of Arts in 1918.

While in attendance at the University of Illinois, he has held the positions of Graduate Assistant (1916-1917), Assistant (1917-1918), Fellow (1918-1919) and Assistant (1919-1920). He enlisted in the Engineer Enlisted Reserve Corps in February, 1918 and received an honorable discharge from that organization in February, 1919.