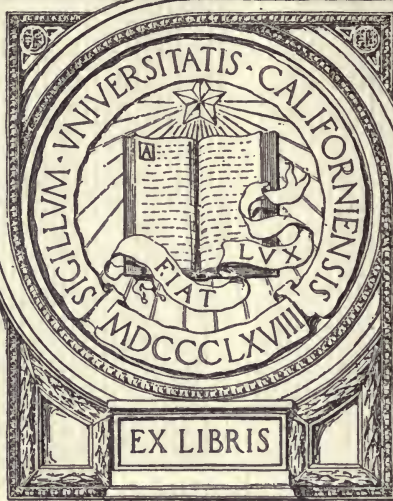


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POTASH IN ILLINOIS SHALES

BY

MINER MANLY AUSTIN

A. B. Lawrence College, 1916

M. A. University of Illinois, 1918

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JUL 19 1922

THESIS



Submitted in Partial Fulfillment of the Requirements for the

Degree of

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

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ACKNOWLEDGMENT

This investigation was carried on in the Chemical Laboratory of the University of Illinois during the years 1918-1920. It was undertaken at the suggestion of Professor S. W. Parr and carried out under his direction.

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. De Wolf, Professor T. E. Savage, and Professor Robert Stewart for the assistance which he has received from them.

Potash Shales of Illinois¹

By M. M. Austin with S. W. Parr

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS,
URBANA, ILLINOIS

Investigation of the potash shales of Illinois was taken up in 1917 in an effort to find values in the residues from certain shales which were under investigation in the laboratory of applied chemistry at the University of Illinois, with primary reference to the amount of oil to be obtained on destructive distillation. The shale from one region, Johnson County, yielded from 45 to 50 gal. of oil per ton and would therefore be of interest for its oil yield alone. Other shales which were of questionable value from the standpoint of oil yield might come into the field of possible technical utilization if other values could be discovered in them. This constituted a primary reason for examining all samples for other values, such as phosphorus and potash. The samples, eighteen in all, were furnished through the courtesy of the Illinois State Geological Survey. They came from localities widely distributed over the state. None of the samples contained phosphorus in more than a trace. Although the majority contained 2 or 3 per cent of potash (K_2O), which is normal for shale rock, two formations showed a potash content of from 5 to 5.8 per cent (K_2O). Of these latter two, the more important is a black carbonaceous shale which outcrops at frequent intervals over a distance of about 7 mi. in Union County. The other is a green sandy shale of entirely different character occurring in Lee County near Dixon, Ill.

POTASH SHALES IN CEMENT MANUFACTURE

From a study of the potash situation it would seem that one of the hopeful sources for a domestic supply resides in the recovery of potash as a by-product from the manufacture of cement. Even though the average shale used in the cement mix does not contain more than 1.5 to 2.5 per cent of potash (K_2O), the potential supply from this source would be very great, as a result of the tremendous tonnage of cement being produced.

The Illinois shales that we are here considering, instead of having an average potash content of 2 or even 2.5 per cent, have a content of 5 per cent. They compare, therefore, very favorably with the greensands of New Jersey.² The first question that naturally arises, therefore, relates to the suitability of these Illinois shales for the purpose of compounding a suitable cement mix

¹ Presented before the Division of Fertilizer Chemistry at the 60th Meeting of the American Chemical Society, Chicago, Ill., September 6 to 10, 1920.

² *Chem. Met. Eng.*, **22** (1920), 815.

Illinois shales of suitable composition for cement making, according to Bleining¹, are shown in Table I. For comparison, two of the high potash shales are shown in parallel columns.

TABLE I—COMPARISON OF ILLINOIS SHALES WITH REFERENCE TO THEIR CEMENT-MAKING PROPERTIES

CONSTITUENT	Average of 8 Illinois Shales (Bleining)	—Illinois Potash Shales—	
		Sample 1	Sample 2
SiO ₂	61.56	53.8	55.0
Al ₂ O ₃	16.12	17.7	16.3
Fe ₂ O ₃	2.96	5.8 ¹	6.0 ¹
FeO	3.52
CaO	0.94	0.7	0.3
MgO	1.79	1.8	1.5
K ₂ O	2.90	5.0	4.9
Na ₂ O	0.82	0.5	0.4
Ignition loss	6.72	11.9	13.0

¹ Total iron calculated to Fe₂O₃.

Samples 1 and 2 are the black carbonaceous shale from Union County. It will be observed that, except in potash content, they vary but little in composition from the average of other shales which are said to be suitable for cement making. Their high potash content might be an advantage also in the formation of the clinker, since it would tend to lower the burning temperature.

Other factors which are important in evaluating these shales for cement-making purposes are as follows:

	Sample 1	Sample 2
Silica-alumina ratio	3.02	3.37
Inert mineral content	0.63	0.75
Sulfur	2.40	2.80

The silica-alumina ratio is in the most advantageous zone, and the inert mineral content is low. The sulfur occurs principally in microscopic form as pyrite.

In average American practice the raw mix will contain 0.7 to 1.0 per cent of K₂O. On the basis of 65 per cent recovery, which according to Huber and Reath² it seems reasonable to expect, there would result an average yield of 2.9 lbs. of potash per barrel of cement. On the same basis, the potash shales whose analyses are given in Table I should yield 5.4 lbs. per bbl.

One other region in the state has thus far supplied a shale with a high potash content, but its cement-making possibilities have not been determined. This shale, from Dixon, in Lee County, contains 5.8 per cent of potash. It is coarse-grained and friable. While its green color is suggestive of the greensands of the East, the geological character of the material is quite different, as will be shown later.

CONSTITUTION OF ILLINOIS POTASH SHALES

The shales from Union County are peculiar in that they contain a small percentage of oil, present in the free state. This has no industrial significance, but it adds to the other volatile constituents, such as water of hydration, so that

¹ Illinois State Geological Survey, *Bulletin 17* (1912).

² *Chem. Met. Eng.*, 16 (1917), 702.

the reduction in weight upon ignition, as shown in Table I, amounts to about 12.5 per cent of the raw material, and the potash content of the residue becomes 5.75 per cent. With the Dixon shale but little loss occurs on ignition, and the potash percentage is about the same in either the ignited or the raw state.

ACTION OF SULFURIC ACID—No very simple or direct method was available for determining the form of combination in which the potash was held. One procedure consisted in digesting 1 g. of the sample with 25 cc. of concentrated sulfuric acid, heating until about half of the acid had been removed, diluting, filtering, washing, and igniting the residue, and analyzing it for total potash. The percentage of potash found was considered as being in some other than the feldspathic form.

By this procedure 62 per cent of the total potash was found to be removed from the Union County shales, while from the Dixon shale only about 15 per cent was removed, showing a marked difference in the chemical composition of the two shales. Further proof of this difference was desired. It is true that in the process of cement manufacture the potash would be equally recoverable in either case; but from any other standpoint differences in the ease with which the potash might be removed by chemical solvents, or concentrated into a form for more ready extraction, might make a wide difference in the value of the shales from the two sources.

It is not the purpose of this discussion to go into the details of the experiments to determine the chemical character of the potash-bearing constituents. The method of analysis suggests that the potash in the Dixon shale is chiefly or altogether feldspathic in combination, and that the major part, at least, of the potash in the Union County shale is in some combination more nearly resembling the glauconitic or greensand formations. These formations are considered as being potassium-iron silicates with an average potash content varying from 5 to 7 per cent K_2O .

MICROSCOPIC EXAMINATION—Thin sections for study under the microscope were prepared. No very positive information came from such studies. In general it seemed evident that the Union County shales had passed through extensive secondary decompositions and that the Dixon shales had not. Both types, however, even in the undisturbed condition of the deposits, had their ultimate particles in such a finely divided state as to render impossible their re-solution and study under the microscope.

TESTS WITH PLANTS—A third method of study into the probable type of composition was as follows: Accepting the generally conceded fact that potash in feldspathic combination is only slightly, if at all, available directly as plant food, further data on composition might be obtained from experiments to determine whether some of the potash in the Union County shales was directly available for plant use. Some foundation for this theory was already afforded by the fact

that 62 per cent of the total potash was soluble in acid. If the Union County shales were treated with strong acid in such a manner as to remove all their acid-soluble potash, and if the residue with the remaining 38 per cent of potash (presumably in feldspathic combination) were submitted to plant action and found lacking in available potash, this would afford a still further proof in the chain of evidence as to the type of potash combination in the original shale.

It is not our purpose to go into the details of the results from these pot cultures, which were conducted by the Agronomy Department of the College of Agriculture, further than to correlate the results, so far as they have a bearing upon the composition of the shales.

In Table II there is shown the behavior of the various shale materials when applied to a peat soil deficient in potash. Buckwheat was selected as the plant most responsive to the varying treatments. An equivalent quantity of potash was added in each case, except to the check pots which, of course, contained no added potash in any form. Each pot was made up of 7 kg. of peat soil, 60 g. of pulverized limestone, and the various types of shale material, ground to pass a 100-mesh sieve, and in an amount that would carry into the soil mixture in each case a total potash content of 1.61 g. (K_2O).

TABLE II—COMPARATIVE STUDY OF BUCKWHEAT GROWTH, USING SHALE MATERIALS OF DIFFERENT COMPOSITION

No.	DESCRIPTION OF POTS	CONDITION OF PLANTS SIX WEEKS AFTER PLANTING
1	Check pot using peat soil with insufficient potash	Poor growth
2	Peat soil as in 1, with Dixon shale	Poor growth, not distinguishable from No. 1
3	Peat soil as in 1, with Union County shale, less 62 per cent of potash by acid extraction	Poor growth, not different from Nos. 1 and 2
4	Peat soil as in 1, with Union County shale ignited	Excellent growth more dense and taller than Nos. 1, 2, or 3
5	Peat soil as in No. 1, with Union County shale, Sample 1 not ignited	Excellent growth, not distinguishable in density or vigor from No. 4
6	Peat soil as in 1, with Union County shale, Sample 2 not ignited	Excellent growth, equal in every respect to Nos. 4 and 5

This amount of potash represents the weight per acre that would be present in a normal soil which was deemed to have an adequate supply of that constituent. The results presented in the table are also clearly shown in the photographic reproduction.

Pot 1 is the check, with deficient potash. Pot 2 has the standard equivalent of 1.61 g. of K_2O added in the form present in the Dixon shale, and Pot 3 has the same addition in the form of acid-insoluble residue from the Union County shale. An examination of these three pots seems to warrant the conclusion that potash in any available form is lacking in each case. This, therefore, would seem to confirm the previous assumption that the potash present in Pots 2 and 3 is in the feldspathic form.

By further reference to Pots 4, 5, and 6, there is an equally



BUCKWHEAT PLANTS GROWING ON PEAT SOIL TO WHICH VARIOUS SHALE MATERIALS HAVE BEEN ADDED

- | | |
|-----------------------------|---------------------------------|
| 1—Check | 4—Union Co., ignited |
| 2—Dixon shale | 5—Union Co., No. 1, not ignited |
| 3—Union Co., acid-extracted | 6—Union Co., No. 2, not ignited |

obvious indication that in these pots potash is present in a form available for plant use; and since the only variable in the experiment is the acid-soluble constituent, it is evident that the potash utilized by the plant comes from this source.

Moreover, ignition or non-ignition of the shale does not affect the property of the potash so far as food availability is concerned. It would be of scientific interest, of course, to be able to say more definitely in what form was the potash combination here found. We have compared it thus far in the discussion to the greensands of the eastern United States which are true glauconites. The most that can be said of these shales is that they are glauconitic in type. They may have been originally a feldspathic deposition which has undergone secondary decomposition *in situ*. Indeed, the region has other striking examples of decomposition, for example, the very pure deposits of amorphous silica, found so abundantly in Union County, as well as some very pure kaolins. So far as conformity to greensand or glauconitic conditions is concerned, there is every justification for such a classification, as may be seen from the following quotation,¹ indicating the geological conditions under which the true glauconites are supposed to have been formed:

The organic matter transforms the iron into sulfide which may be oxidized to hydrate, sulfur being at the same time liberated. This sulfur would oxidize to sulfuric acid, which would decompose clay, setting free colloidal silica, aluminium 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.

Upon analysis of the shale for iron in the pyritic form by methods developed in this laboratory,² it appears that when the pyritic iron is deducted from the total iron of the shale

¹ W. B. Clarke, *J. Geol.*, **13** (1900), 509.

² A. [R.] Powell, with S. W. Parr, University of Illinois Engineering Experiment Station, *Bulletin* **111** (1919).

there remains 3.8 per cent of iron available for combination with the 3.1 per cent of potash present in the acid-soluble form, an amount which approaches the ratio for glauconitic material with sufficient approximation to warrant the classification thus proposed, *viz.*, not true glauconite but glauconitic in type.

We have noted above that some free oil was found to be present in these black shales. It is interesting to speculate as to whether or not in this material, potash feldspar has changed over into shale in the ordinary way, but that the free oil present has prevented the removal of the more soluble materials by an excess of water.

EXTRACTION AND CONCENTRATION OF THE POTASH

The peculiar character of these shales, which seem different from any potash material which the authors have found described in the literature, would seem to warrant a search for some direct method for the extraction of the potash. The facts already presented coupled with the results of other work that we have done preclude the possibility of finding a successful method. Only two-thirds of the total potash content of the rock can be extracted with acids under any conditions. The fine grain and uniform distribution of the potash-carrying constituent make it impossible to bring about any mechanical separation.

CONCLUSIONS

1—In at least two localities in Illinois, shales occur which contain 5 per cent or more of potash.

2—Shale outcropping in several places near Jonesboro, in Union County, which contains 5 per cent 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 lbs. of potash 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, Lee County, contains 5.8 per cent of potash, which is held for the most part in a more stable condition than that in the southern Illinois shale.

6—Extraction of the potassium from shale of either the southern Illinois or the Dixon type by means of solid or liquid reagents would seem to be impracticable, 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 the material of this type outcropping in that locality.

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

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



VITA

The writer of this thesis was born on a farm near Waterloo, Wisconsin, December 19, 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 1919.

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