

THE UNIVERSITY OF MINNESOTA
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of
Committee on Examination

This is to certify that we the
undersigned, as a committee of the Graduate
School, have given Harrison Ashley Schmitt
final oral examination for the degree of
Master of Science

We recommend that the degree of
Master of Science
be conferred upon the candidate.

Chairman

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Date June 7, 1922

THE UNIVERSITY OF MINNESOTA

GRADUATE SCHOOL

Report
of
Committee on Thesis

The undersigned, acting as a Committee of the Graduate School, have read the accompanying thesis submitted by Harrison Ashley Schmitt for the degree of Master of Science. They approve it as a thesis meeting the requirements of the Graduate School of the University of Minnesota, and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science.

W. H. Cummings
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Frank F. Grout

J. W. Geiger

Date June 7, 1922.

AN EXPERIMENTAL INVESTIGATION AS TO THE
POSSIBLE COMMERCIAL PRODUCTION OF
POTASH FROM MINNESOTA ROCKS

A Thesis
Submitted to the Graduate Faculty
of the
University of Minnesota

by

Harrison A. Schmitt, A. B.

In partial fulfillment of the requirements
for the
degree of

Master of Science

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TABLE OF CONTENTS

	Page
Summary and conclusions.....	1
Introduction and acknowledgments.....	3
Age, distribution, and character of the Decorah and Galena formations.....	4
Sampling the Decorah and Galena formations.....	6
Former work on potash in shales.....	8
Preliminary experiments.....	12
Selection of promising experiments.....	16
Extracting potash from the calcareous shale mixed with sodium chloride.....	17
Experimental basis.....	17
Mining and milling for the volatilization process.....	19
Disposal of waste.....	20
Amount and value of the product.....	21
Costs.....	22
Experimentation with potash extraction with brick as a byproduct.....	23
Bomb tests with shale and lime mixtures.....	26
The availability of Decorah shale for use in a portland cement mix.....	27
Use of the Decorah shale as fertilizer.....	28

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AN EXPERIMENTAL INVESTIGATION AS TO THE
POSSIBLE COMMERCIAL PRODUCTION OF
POTASH FROM MINNESOTA ROCKS

By

Harrison A. Schmitt.

SUMMARY AND CONCLUSIONS.

The Decorah in Minnesota is an extensive potash rich shale (6 to 8 per cent K_2O).

The potash is in two forms; about 60 per cent of it more easily available than the rest.

Much potash can be obtained from this shale by heat treatment with equivalent amounts of sodium salts and an excess of $CaCO_3$.

Potash can be rendered soluble and volatilized in part from bricks where salt and $CaCO_3$ have been added to the raw shale.

The Decorah is favorably situated for use with sand if a byproduct from potash extraction is suitable for sand-lime brick as in the greensand process already patented.

The Decorah is also situated near some limestone which may be suitable for portland cement. The Decorah is probably suitable for use in a cement mix.

The Decorah is being tried, with considerable promise

of success, as a fertilizer for potash deficient peat soils which are common near its outcrop.

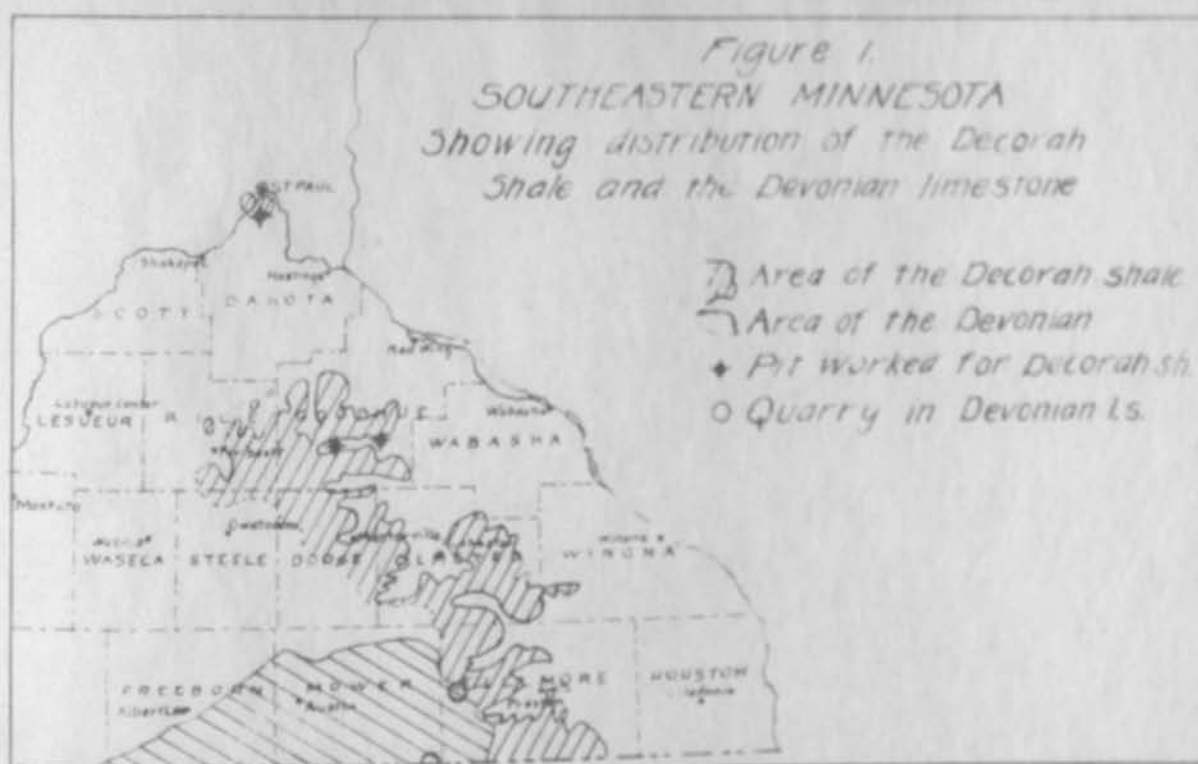
INTRODUCTION AND ACKNOWLEDGMENTS.

It has been known for several years that a certain shale in the State of Minnesota carried an exceptional amount of potash,¹ and the problem studied in this thesis is whether or not this shale has any commercial value because of its potash content and aside from its value for brick manufacture.

The writer is greatly indebted to Dr. F. F. Grout and Dr. W. H. Emmons of the Department of Geology, to Dr. I. W. Geiger of the Department of Chemistry, and to Dr. F. J. Alway of the Department of Agriculture, for criticisms and suggestions.

1 Grout, F. F., Clays and Shales of Minnesota: U. S. Geol. Survey Bull. 678, p. 152.

Figure 1.
SOUTHEASTERN MINNESOTA
Showing distribution of the Decorah
Shale and the Devonian limestone



System	Formation	Thickness	Section	Sample	Character of Rocks
Quaternary	Gray drift	50'			
	Red drift				
Ordovician	Galena ls.	44'		5	Alternating limestone and shale. About 40% limestone
	Decorah sh.	30'		4	Thin lenses of limestone about 14%
		10'		3	No limestone
		10'		2	A little limestone
	Plattville ls.	30'		1	Massive and thin bedded magnesium ls.

Figure 2.
Geologic section of the Decorah shale
Cherokee Heights - St. Paul, Minn.

AGE, DISTRIBUTION, AND CHARACTER OF THE
DECORAH AND GALENA FORMATIONS.

The particular shale in Minnesota known to have a high potash content, the Decorah shale of Ordovician age, has the following position in the Ordovician section as found in Minnesota. (See also plate I., figure 3.)

6. Galena limestone
5. Decorah shale
4. Platteville limestone
3. St. Peter sandstone
2. Shakopee dolomite
1. Onecta dolomite.

The Galena limestone directly above the Decorah has many potash rich shale layers.

The distribution of the Decorah formation shown on the map (see plate I., figure 1), is that part of the formation either outcropping (shown by the heavy line on the map), or is covered by a small overburden of drift (limited by the dotted line on the map). It does not include that part of the shale covered by other rock formations such as the Devonian in the south part of the State.

The Decorah formation becomes thinner toward the south and west, except at Cannon Falls, Minnesota, where it is thicker. The amount of included limestone increases toward the south and west.

Though no sampling has been done outside of the St. Paul outcrop, which is the northernmost extension of the formation, the potash content is probably high for some distance south, for the shale has about the same character and makes the same quality brick.

The outcrop from which samples were taken for this thesis is part of an erosional outlier located at Cherokee Heights, St. Paul. (See plate I., figure 1.) Here the shale outcrops for several miles along the Mississippi river.¹

The whole area, including that in which the shale outcrops and that in which it is drift covered, is a part of the State well farmed, thickly populated, and readily accessible by a network of railways and good roads. There should be no trouble encountered in locating large bodies of shale near transportation facilities.

The Decorah formation at St. Paul has a thickness of about 60 feet, 50 feet of this being green clay shale and with 10 feet of low magnesium limestones. These limestones are in thin lenticular layers, increasing in thickness and number toward the top until they merge into the Galena formation.

"The Decorah is everywhere color-banded but is not laminated or fissile except along some calcareous layers. When

1 See also, Sardeson, F. W., U.S. Geol. Survey Folio 201, Minneapolis-St. Paul.

fresh it is green but weathers to buff or brown. On exposure it breaks with a cuboidal fracture and weathers to clay in a single season."¹

The Galena formation, only 40 feet thick here due to glacial erosion, has much the same character as the upper part of the Decorah where the limestone lenses are thicker. In the Galena the limestones are still thicker and make up about 50 per cent of the formation. The other 50 per cent is shale of the same character as that in the Decorah and with the same high potash content.

The drift over-burden, which is about 50 feet thick here, is unconsolidated gravel, sand, and boulder clay.

SAMPLING THE DECORAH AND GALENA FORMATIONS.

Most of the preliminary experimental work was done on a sample from the lower layers of the Decorah. It was sampled by Dr. F. F. Grout. It presumably contained no limestone, for the analysis shows less than one per cent of CaO. (Plate II., figure 1, analysis number A.)

After preliminary results on this sample had shown some promise, the whole geologic section exposed, including the

1 Sardeson, F. W., U.S. Geol. Survey Folio 201, Minneapolis-St. Paul.

Decorah shale and part of the Galena formation, was carefully sampled vertically. (See plate I., figure 2, samples number 3, 4, and 5.) The lower 10 feet of the Decorah immediately above the Platteville limestone was not accessible at the time the samples were taken, so that part of the section remained unsampled.

Sample number 3 included a total of 10 feet of vertical section in the lower pure shale. It was taken at the freshly worked face of a drift which ran horizontally into the formation and at right angles to the outcrop. The sampling, in this case, was done by channeling and dropping the material onto a sampling cloth.

The next 30 feet of the section was sampled at the outcrop and on a nearly vertical face where mining was actively going on. The elevation was checked up by a line of levels run into the drift to which reference was just made. No sampling cloth could be used on this face, so by estimation two pounds of material were knocked out of the face for every foot of vertical distance progressing upward toward the top, and this thrown into a bag carried by the sampler.

The upper 44 feet, mostly Galena formation, was sampled in the same way.

All the samples were broken up to pass one-half inch mesh and then quartered. The total final weight of the samples was equivalent to a pound per foot of vertical section, or about

	A	B	C	D	*3	*4	*5	*6
SiO ₂	55.71	56.35	54.66	50.81		38.37	35.93	37.87
Al ₂ O ₃	2.052	1.863	2.404	2.025		22.06	13.88	14.23
Fe ₂ O ₃	4.54	6.19	6.53	5.18		↑↑	↑↑	2.97
FeO	↑	↑	↑	↑		↑	↑	1.63
MgO	2.88	2.97	1.08	2.13		5.77	4.05	3.29
CaO	96	96	45	4.05		10.87	20.98	14.73
Na ₂ O	33	25	47	28				43
K ₂ O	6.20	7.37	5.37	5.69	8.24	6.44	5.04	5.96
H ₂ O+	7.70	4.81	5.15	8.92		16.50	19.58	2.67
H ₂ O-	↑↑	2.41	2.35	2.16		↑↑	↑↑	1.25
CO ₂	↑	↑	↑	↑		↑	↑	13.94
TiO ₂	57	65	.66	50				45
P ₂ O ₅						3.47	2.85	2.83
S						10	10	10

99.41 100.59 100.76 99.97 100.36 99.75 99.80
 A Lower layers *3 See Plate I figure 2
 B *4
 C ? *5
 D Upper layers? *6-*3,*4, and *5 combined
 B, C and D - F. F. Grout analyst. A, *3, *4, *5, *6 - H. Schmitt analyst.

Figure 1.

Analyses of the Decorah shale

	A	B	C	D
Insol				
SiO ₂	11.41	20.40	13.19	20.38
Al ₂ O ₃				26.77
Fe ₂ O ₃				1.57
FeO	1.38	3.40	2.70	
P ₂ O ₅				
TiO ₂				
MgCO ₃	6.39	26.44	29.98	11.18
CaCO ₃	77.42	45.76	46.15	41.90

Figure 2.
 Analyses of the Plattville limestone

A, B and C - Analyses by Minneapolis Crushed Stone Co.

D - Analyst?
 A Quarry floor to 85' above
 B 8.5' to 16'
 C 16' to 24'
 D Overlying crumbling rock.

94 pounds altogether.

After careful weighing of the three separate samples, a fourth sample (number 6) was made up as a fair sample of the whole section by combining parts of the first three samples (numbers 3, 4, and 5) in proper proportion of weight to vertical section represented by each.

Finally, the four samples were ground to an impalpable powder in a ball mill.

Partial or complete rock analyses were run on all the samples (see plate II., figure 1.).

FORMER WORK ON POTASH IN SHALES.

It has not been generally known that some clays and shales have exceptionally high potash content, the average being 3.24 per cent,¹ and as a consequence during the last few years of frenzied search for potash in this country, shales and clays were almost entirely neglected, except where they were the source of potash byproduct in the portland cement industry. However, slates and phyllites have received some attention.²⁻³

A good deal of work has been done in trying to extract,

1 Gale, H. S., Mineral Resources 1916, U.S. Geol. Survey, pt. II., p. 119.

2 Gale, H. S., Mineral Resources 1916, U.S. Geol. Survey, pt. II., p. 123.

3 Gale, H. S., and Hicks, W. B., Mineral Resources 1917, U.S. Geol. Survey, pt. II., p. 441.

profitably, potash from orthoclase. The U. S. Geological Survey has shown that the average potash content of orthoclase seldom runs over 7.5 per cent.¹ It is noteworthy that the Decorah shale separated from the limestone carries well over 7 per cent of potash and in a much more available form than in orthoclase. Furthermore, the shale is obviously much easier to mine and grind than orthoclase, and is in unlimited quantities, whereas commercial orthoclase is limited to pegmatite deposits, the majority being comparatively small.

Previous experimentation which has been done with clays and shales for potash has been along the following lines:

1. Extraction of potash from flue dust of cement kilns.

2. The Cowles process (patented) designed to extract alumina from clay, with hydrochloric acid and potash as byproducts.² In this process a mixture of salt and clay is pressed into bricks and heated in the presence of superheated steam, whereby HCl is given off and alkali-silico-aluminate formed; this compound is then decomposed by heating with limestone to form lime silicate, a soluble alkali-aluminate being left.

3. In a process outlined by A. W. Heyman³ a calcareous

1 Hicks, W. B., Mineral Resources 1918, U.S. Geol. Survey, pt. II., p. 408.

2 Phalen, W. C., Mineral Resources 1915, U.S. Geol. Survey, pt. II., p. 115. Also see U.S. patent 1,111,881.

3 Phalen, W. C., Mineral Resources 1915, pt. II., p. 121.

mixture (containing potash in clay, shale, orthoclase, etc.), either natural or artificial, is heated to 900-1600° C. The hot material, or the ground cold material, is treated with water and the hydroxide of potash extracted from this solution. The residue may be used for cement manufacture.

4. Clay, salt and calcium carbonate when heated together give water soluble potash.¹

5. U. S. patent 521,712. Clay, $(\text{NH}_4)_2\text{SO}_4$ and K_2SO_4 are heated together and the potash leached from the frit.

6. U. S. patent 1,123,693. Feldspar and clay are heated in the presence of NaCl and H_2O . Soluble K_2O is extracted.

7. U. S. patent 1,236,903. Slate, shales, etc., are furnaced with limestone the the potash volatilized.

8. The study of the availability of potash in shales for plant food.²

Previous work on clays and shales has shown:

1. That potash recovery from cement manufacture is a commercial success.

2. That methods of extraction of potash from silicate rocks primarily for recovery of potash, and with no byproduct produced, probably will not be commercially successful.

1 Chem. Abs. 13, p. 1625. See also U.S. patent 1,297,078.

2 Austin, M. M., and Parr, S. W., Potash Shales in Illinois: J.I.E.C., vol. 13, pp. 1144-1146.

3. That high potash shale may make a valuable fertilizer; preliminary pot tests showing phenomenal results,¹ but with preliminary field tests showing negative results.

Previous work, from a chemical standpoint, on potash recovery from silicate rocks (including clays and shales) has shown:

1. That under certain conditions, when lime is intimately mixed with silicates carrying potash, an exchange of bases occurs, potash being released from its previous combination. This point is fundamental and the basis for many processes of potash extraction.

2. That HF, concentrated H₂SO₄, and other acids will decompose certain silicates containing potash, the potash becoming soluble in the acid.

3. Pulverizing and heating makes some potash water soluble in some rocks such as alunite.²

4. Water and CO₂ under high pressure and temperature decompose some silicates.

Nearly all processes for potash extraction from silicate rocks (including clay, shale, slate, and phyllite) with a few exceptions are based on one or more of the four principles outlined above.

1 Univ. of Ill. Agric. Exp. Station Bull. 232, p. 229.

2 Nourse, M. R., Mineral Resources 1920, U.S. Geol. Survey, pt. II., p. 106.

PRELIMINARY EXPERIMENTS.

In doing the preliminary experiments it was constantly kept in mind that it was worth while to use only reagents and processes which are cheap and easily available. Many methods for the quantitative extraction of potash in the laboratory are known. The problem was not merely one of extracting potash, but to find the method or methods that might prove commercially feasible.

Many methods for actual quantitative determination of the potash were used depending on conditions and interfering substances present in each experiment. Blanks were run on all reagents where necessary. Percents of potash were in all cases based on the air dried sample and not on the ignited residue. The percents reported on certain Illinois shales were based on ignited residue where loss on ignition was as much as 20 per cent. These percents were the highest reported, 5.8 and 5.75. The per cent in the air dried samples was somewhat less.

The first thing done was to determine the amount of K_2O in the shale sample to be used. The average of four determinations gave 6.20 per cent (see plate II., figure 3, analysis A for complete analysis).

A brick made from the shale, by the Twin City Brick Company, Cherokee Heights, St. Paul, was analyzed. It carried 7 per cent K_2O . This was significant as it showed that very

little potash, if any, was volatilized by burning in the kiln. Shrinkage would account for the fact that the K_2O content is higher than that for the shale average. The kiln temperature used at Cherokee Heights is about $1000^{\circ} C$. This temperature should be ample to volatilize any free potash during the three day burning. A later analysis of the flue dust from the kilns showed a water soluble K_2O content of 1.26 per cent, so a slight amount of potash seems to be volatilized. Other experiments should be made with flue dust. It may be practicable to precipitate the flue dust from the kilns by the Cottrel method of electrical precipitation or by some other method, and to leach out the water soluble potash, small as the amount is. Flue dust from cement kilns with as low as 2 per cent K_2O is saved and sold¹.

Some fragments of the brick carrying potash, before analyzed, were boiled for a half hour in water. Not even a trace of potash was extracted.

A trace of potash was extracted from the same fragments by boiling with dilute HCl.

Ground shale was heated at $1000^{\circ} C$. for 3 hours. There was a loss of 8 per cent of the total potash content.

NaCl was substituted for NH_4Cl in the same proportion to sample and $CaCO_3$ 1:1:8 as in the J. Lawrence Smith method for

1 Hicks, W. B., Mineral Resources 1918, U.S. Geol. Survey, pt. II., p. 407.

quantitative determination of the alkalies and the sintering carried on as in that method. All the potash became water soluble. To make sure that this reaction was not entirely due to CaCO_3 , a "sintering" was made without using NaCl . Only 4 per cent of the potash present became water soluble. Then no CaCO_3 was used in a "sintering". The extraction was only 2 percent. Then NaCl , a fifth of the weight of the sample, was used instead of an equal weight, as at first. The extraction was reduced to 85 per cent of the total potash present. In turn the CaCO_3 was reduced to a fifth of the original amount used. The extraction was 75 per cent of the total potash present. It seemed clear that both NaCl and CaCO_3 were necessary for complete extraction.

Several experiments were tried substituting sodium compounds other than NaCl for NH_4Cl in the J. Lawrence Smith method. The results were:

Compound substituted	Potash extraction
NaOH	88.%
Na_2CO_3	83.%
Na_2SiO_2	00.%

No further test substituting other salts, bases, etc., was made. Results along that line would be interesting as they would help clear up the question as to just what are the reactions involved. Probably only the negative radical is essential and many hydroxides, carbonates, and chlorides will give similar

results.

Austin and Parr¹ found that an Illinois shale high in potash gave high extraction with concentrated H₂SO₄. This experiment was duplicated. One gram of shale was digested with 25 cubic centimeters of H₂SO₄ until one-half the acid was fumed off. The extraction was 60 per cent. Evaporation to dryness gave an extraction of 62 per cent. The amount of extraction agrees closely with that of the Illinois shale. These and other experiments tend to confirm Austin and Parr's findings that the potash is held in two forms, one of them probably feldspathic. Just in what form of combination the rest of the potash (the 60 per cent) is in is a problem not easily settled because of the submicroscopic character of the shale particles. It seems reasonable to suppose that the more soluble part of the potash is held in combination by various zeolites of indefinite composition as seems to be the case in soils.²

1 Austin, M. M., and Parr, S. W., Potash Shales in Illinois: J.I.E.C., vol. 13, pp. 1144-1146.

2 Snyder, Soils and Fertilizers, p. 155.

SELECTION OF PROMISING EXPERIMENTS.

After the preliminary work just described and after a survey of the literature on potash extraction by commercial or would-be commercial methods, it was decided to concentrate on five lines of attack. These were as follows:

1. The extraction of volatile or soluble potash using shale, salt, and CaCO_3 .
2. Using the same materials and attempting to get brick as a byproduct.
3. Experiments with CaO , shale and water under pressure and heat with the idea of getting KOH and also a lime residue for use in making sand lime brick as a byproduct.¹
4. The possibility of using the shale in a portland cement mix.
5. The possibility of using the shale as a fertilizer.

1 Charlton, H. W., Recovery of Potash from Greensand: J.I.E.C., vol. 10, pp. 6-8.

EXTRACTING POTASH FROM THE CALCAREOUS SHALE
MIXED WITH SODIUM CHLORIDE

Experimental Basis

The most promising method for direct extraction of the potash seems to be either (1) rendering the potash water soluble by mixing the ground shale and the included limestone with common salt and heating to about 800° C., or better (2) heating the same mixture to 1150° C. and thus volatilizing the potash.

On plate III. are curves worked out showing the amount of extraction of potash in percents where the amounts of shale and CaCO_3 are the variables and the amount of NaCl is kept constant. One curve shows the amount of potash (K_2O) made water soluble at 800° C. while the other shows the amount volatilized at 1150° C.

It was later found that the same results as shown by the curves could be gotten by using much smaller amounts of NaCl . The equivalent amount of NaCl to the amount of K_2O present plus a slight excess is always sufficient, at least for the volatilization curve.

However, these curves do show the intimate relation of the per cent of potash extraction to the per cent of CaCO_3 present. The "flattening" out of the curve in figure 1 is probably due to the fact that the potash is held in two sorts of combina-

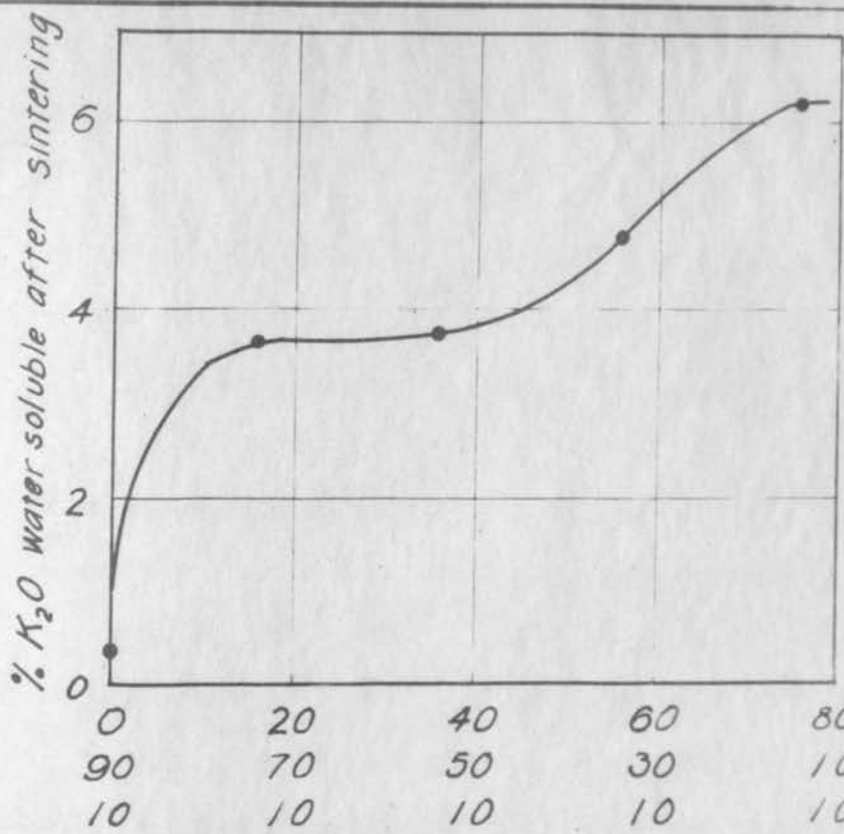


Figure 1.

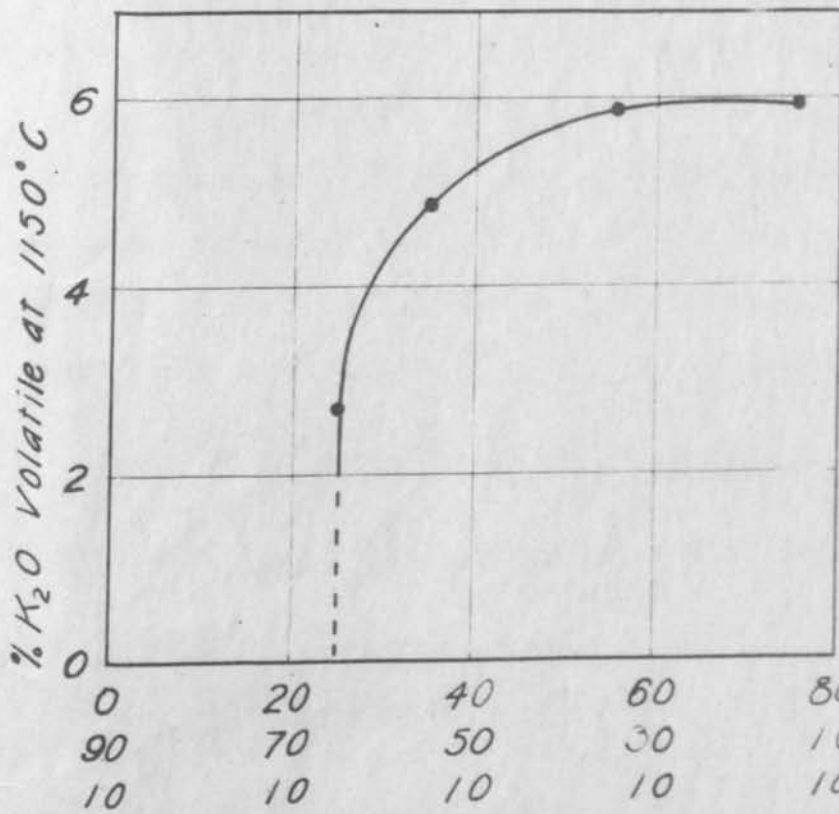


Figure 2.

Curves showing in per cents the amount of potash water soluble after sintering at 800°C and the amount volatile at 1150°C with varying proportions of shale and CaCO₃. The NaCl kept constant.

tion, one of them more resistant to decomposition than the other, as was brought out by the concentrated H₂SO₄ experiments.

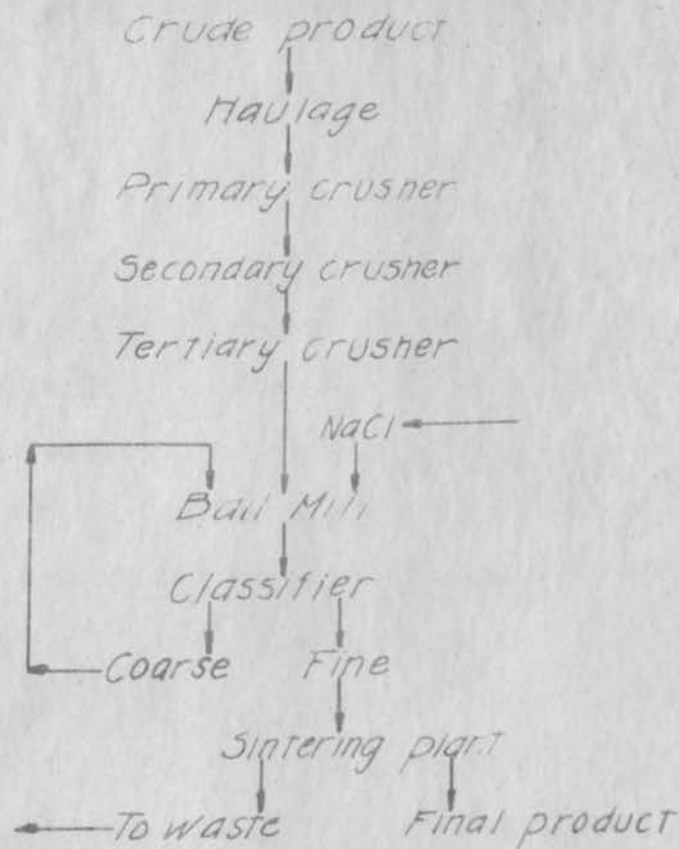
Fusion occurs where the CaCO₃ is below 25 per cent and the temperature above 1150° C. The writer is of the opinion that the downward break in the curve for volatile potash, which is mainly due to fusion, could be somewhat flattened out by heating at a slightly lower temperature for a longer period of time. This was actually done in later experiments with samples numbers 4, 5, and 6, with the result of increasing the per cent of volatilization above the amount to be expected by reference to the curve and by consideration of the CaCO₃ present.

The following table gives (1) the per cent of CaCO₃ in each sample, (2) the per cent of K₂O in each sample, (3) the per cent of NaCl used, (4) the volatilization estimated by reference to the curves, (5) the actual volatilization obtained by experiment, and (6) the per cent of K₂O volatilized.

Table showing potash volatilized from different samples.

Sample	1 CaCO ₃	2 K ₂ O	3 NaCl	4 Estimated Vol- atilization	5 Actual Vol- atilization	6 Per cent of total vol- atilized.
4	19.40	6.44%	10%	0.00%	3.26%	50.62%
5	37.45	5.04	10.	4.18	5.04	100.00
6	26.29	5.96	10.	3.36	4.81	80.70

The discrepancy between the amount actually volatilized and that expected to be volatilized is explained, as before noted, by the longer heating at a slightly lower temperature which these



FLOW SHEET
 FOR
 Potash extraction plant
 Utilizing the Decoran Shale
 as a source of potash

samples received.

Sample number 5 gives complete volatilization. Under carefully regulated conditions of mining and milling the volatilization efficiency of the material represented by sample number 6 could also be brought to 100 per cent. Thus in mining it would be simple enough to mine some of the Platteville limestone along with the Decorah and Galena formations and thus increase the CaCO_3 content. Farther south the amount of included limestone is greater and perhaps additional limestone would not need to be added to obtain complete recovery.

Though no actual quantitative analyses of the sublimate from the above mixtures were made, qualitative and physical tests showed that most of the potash came off as KCl with some NaCl as impurity. Possibly some potash comes off as K_2O . In any event, the sublimate is water soluble and practically pure.

Mining and Milling for the Volatilization Process

The open pit method would be used for mining the Decorah and Galena formations. Stripping the drift would be done by steam shovel for large scale operations. The actual mining would also be done by steam shovel.

The milling processes necessary are outlined by the flow sheet (plate IV.). The process starts with primary crushing and then successive crushing until the material is finally ground to an impalpable powder in a ball mill. Probably tertiary

crushing and possibly secondary crushing could be done away with in grinding such soft material.

The addition of salt would take place ahead of the ball mill, thus causing thorough, intimate mixing and grinding.

The sintering process would present a difficult mechanical problem and is a possible stumbling block for the whole process. The writer believes that a furnace fitted up with long cast iron cylinders, jointed if necessary, with a screw arrangement inside so as to keep the material moving continuously from the head end to the tailing end, could be designed. Outlets leading to precipitating chambers would be provided at intervals for the KCl sublimate. A system of preheating would best be used. That is, the hottest part of the furnace should be near the tailing end of the cylinders while the head end would be preheated by the cooler gases.

Disposal of Waste

It is questionable whether any use could be made for the tailings. The calculated composition of the tailings is as follows. It is based on the processing of representative sample number 6. Na_2O is considered replacing K_2O . Sulphur may or may not be lost on sintering.

SiO ₂	47.29
Al ₂ O ₃	17.75
Fe ₂ O ₃	5.97
FeO.....	
MgO.....	4.10
CaO.....	18.40
Na ₂ O.....	5.43
K ₂ O.....	0.00
H ₂ O+.....	0.00
H ₂ O-.....	0.00
CO ₂	0.00
TiO ₂56
P ₂ O ₅35
S.....	.12

99.97

If the process was regulated so that the tailings were just agglomerated as they left the furnace it might be possible to use them as a road material. Otherwise the disposal of such tailings would probably be a considerable item of expense.

Amount and Value of the Product

On the basis of volatilization of all the potash from representative sample number 6 using 10 per cent added limestone the potash (K₂O) produced would be 5.41 per cent of the raw material treated. This would be equivalent to the production of 215 pounds of 80 per cent muriate¹ per short ton of shale treated.

¹ The standard concentration of muriate. The other 20 per cent is NaCl.

$$\frac{2000 \times .0541 \times \frac{2KCl}{K_2O}}{.80} = 215.72$$

Based on prices for muriate existing from 1911-1914 this amount would be worth about \$5.75 F.O.B. St. Paul, Minnesota. This is the gross value of the product per ton of shale and limestone treated.

Costs.

The simplest and most accurate way of estimating costs for a prospective enterprise is to compare it with a going industry using similar materials and processes. In this case the obvious comparison is with the portland cement industry.

Rough estimates using this industry in comparison to the potash volatilization process seem to show that a reasonable profit could be made where the industry would be operated on a large scale basis. That is to say, where 500 tons or more of raw material would be treated per day.

EXPERIMENTATION WITH POTASH EXTRACTION WITH
BRICK AS A BYPRODUCT.

It was thought that perhaps by taking advantage of the water soluble and volatile features where NaCl was added to the calcareous clay,¹ bricks could be made, and that either water soluble potash could be leached from the finished product or that the bricks could be burned at a high enough temperature to volatilize all the potash. Enough work was done with bricks to show that this is a very promising line of attack on the problem. These first results show that where high lime is present (10 to 20 per cent CaO) satisfactory brick can only be produced at about 800-900° C. and that these bricks are of a common building grade. Further, that a combination of the water soluble and volatile features would give the greatest efficiency of extraction at the temperature burning the best brick (between 800° and 900° C.). Within this range of temperature some potash would be volatilized, but some would remain water soluble in the brick and would have to be leached out after the brick had cooled. It is possible and probable, however, that under actual conditions of burning where a kiln temperature of say 850° C. was maintained for two or three days practically all the potash would be volatilized.

1 The artificial calcareous or limey clay mixture.

That is, all the potash released with that particular lime and shale mixture. The results of long period, low temperature burning are not known. It seems reasonable to expect that any water soluble potash remaining in the brick after a short time of burning would be completely volatilized after a longer duration of burning.

The actual laboratory experiments were not extensive and much further work is necessary to show the exact status of this phase of the potash problem.

In the laboratory briquettes were made from each of the samples numbers 4, 5, and 6. During mixing 10 per cent NaCl was added to each sample. The NaCl and the samples had been ground to an impalpable powder. As little water as possible was added to make the clay plastic, so as to prevent efflorescence of the NaCl during drying. Preliminary tests on the unburned clay and bricks gave the following results. These results are approximate and are for all three mixtures used.

Water of plasticity	25 per cent
Plasticity	very plastic
Tensile strength of dried bricks	100 pounds
Linear air shrinkage	6 per cent.

Then 3 briquettes were burned for each sample with the following results:

Results of burning shale samples with the addition of salt.

	Temperature Centigrade	Color	Remarks	K ₂ O	
				Volatile	Soluble
			<u>Sample #4</u>		
1	750	Salmon	fair common grade		
2	850	do.	do.		
3	1110	Buff	incipient fusion		
			<u>Sample #5</u>		
1	750	White	good common grade		
2	850	Salmon	do.		
3	1110	Buff	incipient fusion		
			<u>Sample #6</u>		
1	750	White	poor common grade		
2	850	Salmon	good common grade		2.91
3	1110	Buff	incipient fusion	3.46	

BOMB TESTS WITH SHALE AND LIME MIXTURES.

Several tests were made with clay and CaO mixtures in a bomb, attempting to duplicate conditions under which potash has been extracted from greensands. In the process described by H. W. Charlton¹ a lime sludge byproduct is obtained suitable for use in the manufacture of sand-lime brick. He placed greensand, CaO and water, in certain proportions, in an autoclave and brought to high pressures and temperatures. The potash in the greensand became water soluble in the form of KOH and could be filtered from the sludge.

This experiment was duplicated, substituting shale for greensand. The proportions of the constituents were the same as those recommended as most favorable for greensand. These proportions were, shale 1 part, CaO 0.9 part, and water 5 parts. The temperature was 238° C. giving a pressure of 438 pounds per square inch in the bomb. The time of heating was 4 hours.

On testing the residue it was found that the extraction in one case (the highest) was 3.5 per cent K₂O or 56 per cent of the total potash present.

Since in this case the shale had not been previously finely ground and some of it was still in lumps on opening the

1 Charlton, H. W., Recovery of Potash from Greensand: J.I.E.C., vol. 10, pp. 6-8.

bomb, and since there was evidently not enough water present, for the residue was dry, it is thought that by using finely ground shale and by increasing the water content the extraction could be considerably increased.

If this method were used for potash extraction and the sludge were suitable for sand-lime brick manufacture, the St. Peter sandstone would be an excellent source for the sand used in the brick, since white silica sand is needed. This sand has been actually tested and makes satisfactory sand-lime brick.

THE AVAILABILITY OF THE DECORAH SHALE FOR USE
IN A PORTLAND CEMENT MIX.

In average American practice a shale or clay is considered suitable for cement manufacture when the silica-alumina ratio falls between 2.5-3.5.¹ This ratio for the pure shale is 2.71. Sample A was used for the ratio (plate II., figure 1).

$$\frac{55.71}{20.52} = 2.71$$

If limestone three times the weight of the shale is considered necessary to compound a suitable cement mix, on the

1 Austin, M. M., and Parr, S. W., Univ. of Illinois Agr. Exp. Sta. Bull. 232.

basis of a 66 per cent recovery from sample A, the recovery per barrel of cement would be 5.28 pounds in comparison to 2.9 pounds, the average recovery for American practice. If the shale represented by sample number 3 were used, the recovery of potash would be correspondingly higher.

There is a possibility that the Devonian in the south part of the State contains commercial quantities of cement rock. If such a deposit exists and a cement industry could be located there, the Decorah shale could be profitably used in the cement mix. The shale outcrop is only a short distance from the Devonian. (See plate I., figure 2.)

USE OF THE DECORAH SHALE AS FERTILIZER.

Preliminary pot tests by the Agricultural Experiment Station of the University of Illinois showed that the potash content in a certain Illinois shale gave phenomenal results as a fertilizer.¹ Some of the potash in the shale, though it was not water soluble, was evidently more available for plant food than the water soluble potash in commercial fertilizer. Field tests made with this Illinois shale showed negative results. They should be checked.

1 Austin, M. M., and Parr, S. W., University of Illinois Agr. Exp. Sta. Bull. 232.

As before mentioned, there is close correspondence between the percents of K_2O sulfuric acid soluble in the Illinois and Minnesota shales.

This indicates that some of the potash in the Minnesota shale is in the same sort of combination as some of that in the Illinois shale. Therefore, it is believed that the Minnesota shale will not only show beneficial results as a fertilizer in pot tests, but will have certain advantages for field use that the Illinois shale did not have and which may make it beneficial in the field.

There are certain difficulties connected with the use of the Illinois shale.

1. It carries about 40 gal. of oil to the ton, which makes it difficult to grind finely on a large scale as for field application. Applied without fine grinding as was done in the field tests referred to, it does not slack down and become disseminated. It seems as though this was the cause of its unavailability as plant food.

2. The potash content of the raw shale is only 5 per cent.

3. Its distribution is limited, the outcrop being only 10 feet wide. The stratigraphic thickness is less than 10 feet.

In contrast, the Decorah shale has these advantages:

1. It is easily ground up.

2. It slacks down on one season's exposure, so it would

not need to be ground up at all if left exposed for a year.

3. Its potash content is over 8 per cent in one 10 foot layer, while the whole formation thickness of 100 feet including the Galena formation carries nearly 6 per cent K_2O .

4. It carries limestone in large amounts which would increase its value as fertilizer on lime deficient soils.

5. The formation is extensive, thick, and easily available.

6. It is near great acreages of potash deficient peat soils.

It is noteworthy that peat soils are not only usually potash deficient but also clay deficient.

If 60 per cent of the potash of the 8 per cent shale was available for plant food, a dressing of one ton of shale to the acre would be equivalent to a top dressing of 175 pounds of 80 per cent muriate. This is a little more muriate than is usually applied.

Field tests using some of the Decorah shale richest in potash will be made this summer (1922) by Dr. F. J. Alway, Chief of Division of Soils, College of Agriculture, University of Minnesota. These tests will be conducted at Anoka, Minnesota.