room by a drying tube not shown in the figure. It is filled with pieces of stick caustic potash broken to the size of a pea.

LABORATORY OF THE PARK STEEL WORKS,
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PITTSBURG, PA.

(CONTRIBUTION FROM THE OFFICE OF PUBLIC ROADS, U. S. DEPT. AGRICULTURE.)

THE EXTRACTION OF POTASH FROM FELDSPATHIC ROCK.[1]

BY ALLERTON S. CUSHMAN AND PREVOST HUBBARD.

Received March 4, 1908.

The extraction of potash from native rocks has long been considered one of the most important as well as one of the most difficult problems of industrial chemistry. In spite of the enormous resources of the North American continent, there has not yet been found anywhere on it an available source of potash, thus necessitating the importation from abroad of many hundreds of millions of pounds per annum of the salts and compounds of this important substance. One result of this lack of a native source of supply has been to stimulate the use in agriculture of hard wood ashes, which are even at the present time brought from Canada in considerable quantities to the added devastation of the fast disappearing forests. In addition to this, cotton hull ashes from the South are shipped to the North, which merely robs the soil of one portion of the country to supply the deficit in another. The pegmatitic granites and feldspathic dykes of the eastern and central western United States offer an unlimited source of supply which only awaits an economical method for making it available. Many of these feldspar deposits run as high as 10 per cent. in potash (K_2O) and it follows, therefore, that a quarry only fifty feet square and fifty in depth contains about 2,000,000 pounds of this alkali. Under the stimulus of the rapidly growing cement industry, great advance has been made in the last few years in the art and economics of fine grinding, which must of necessity be the first step in any process which attempts the extraction of potash from feldspar or other minerals. At the present time, in the manufacture of Portland cements, at least two extremely fine grindings as well as a burning at a high temperature are accomplished so economically that the finished product can be packed in bags or barrels and sold in some places for a price equal to about three-tenths of a cent per pound or about six dollars per ton. In view of the fact that a short ton of 10 per cent. feldspar contains about ten dollars' worth of potash at prevailing prices the problem of extraction is not on first thought an unpromising one from an economical standpoint.

There are about twenty well defined rock-forming minerals as com-

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[1] Paper read before the N. Y. Section, Am. Chem. Soc., Feb. 7, 1907. Published with the permission of the Secretary of Agriculture.

prised in the following tabular list, only a few of which, however, may be considered as possible sources of raw material. Of these orthoclase and microcline are probably the most important. The potash feldspars occur in large dykes or deposits in various parts of the country, and have been particularly developed in Maine, Connecticut, New York, Pennsylvania and Maryland, where they are mined and ground for use almost exclusively in the ceramic industries. Many of these pegmatite deposits, however, because of insufficient coarseness, too large a percentage of quartz, or too great an abundance of iron-bearing minerals, are unfitted for finer uses and therefore are especially available as a raw material for potash extraction.[1]

POTASH-BEARING SILICATES ARRANGED ACCORDING TO DANA.

ORTHOSILICATES.

Kaliophilite: Silicate of alumina and potash. K_2O, 27.20–29.30 per cent.

Microsommite: Sulpho-silicate of alumina, lime, soda, and potash. K_2O , 6.25–7.82 per cent.

Nephelite: Silicate of alumina, soda, and potash. K_2O, 4.55–7.14 per cent.

Hauynite: Sulpho-silicate of alumina, lime, and soda (potash). K_2O, 0.33–4.96 per cent.

Algerite: Silicate of alumina, magnesia, and potash, and water with some $CaCO_3$. K_2O, 9.97 per cent.

METASILICATES.

Leucite: Silicate of alumina and potash. K_2O, 18.90–21.48 per cent.

POLYSILICATES.

Orthoclase: Silicate of alumina and potash. K_2O, 5.40–15.99 per cent. Constitutes at least 15 per cent. of the earth's crust and occurs in nearly all varieties of acid igneous and metamorphic rocks, as well as in many sandstones, conglomerates, etc.

Microcline: Same as orthoclase, except as to crystal habit.

Hyalophane: Silicate of alumina, baryta, and potash. K_2O, 7.82–11.71 per cent.

Anorthoclase: Silicate of alumina, lime, soda, and potash. K_2O, 2.50–11.90 per cent.

HYDROUS SILICATES.

Muscovite: (White or potash mica) silicate of alumina and potash. K_2O, 6.83–11.10 per cent.

Lepidolite: (Lithia mica) fluoro-silicate of alumina, lithia, and potash. K_2O, 10.78–12.34 per cent.

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[1] See *Mineral Resources of the U. S., 1906.* E. S. Bastin.

Zinnwaldite: (Lithia mica) composition like lepidolite but contains iron. K_2O, 10.46–10.58 per cent.

Biotite: (Iron or black mica) silicate of alumina, magnesia, iron and potash. K_2O, 6.18–10.08 per cent.

Phlogopite: (Magnesia mica) silicate of alumina, magnesia, and potash. K_2O, 7.06–10.32 per cent.

Lepidomelane: (Black mica) silicate of alumina, iron and potash. K_2O, 6.06–9.45 per cent.

Roscoelite: (Vanadium mica), silicate of vanadium, iron, magnesia, alumina and potash. K_2O, 7.59–8.87 per cent.

Zeolites: Hydrous silicates of alumina, lime, soda, run from traces to 11.09 per cent. K_2O. The principal potash-bearing varieties are *Phillipsite* (0–11.09 per cent. K_2O), *Chabasite* (0–4.39 K_2O), *Analcite* (0–2.83 per cent. K_2O), and *Natrolite* (0–1.17 K_2O).

The question of the use in agriculture of very finely ground feldspar without any further treatment has previously been discussed by one of us,[1] and systematic experiments are being carried on year by year by the Department of Agriculture in order to test the value of potters' feldspar ground to 200 mesh as a tobacco fertilizer. It has been pointed out that by grinding the spar, either dry or in the form of a slurry with lime, ammonium salts or gypsum, the potash can be made more quickly available to plants.[2] It is an interesting question whether these simple methods could not be developed in order to prepare feldspathic rock for use in agriculture.

The principal representatives of the potash soda feldspar group, orthoclase and microcline, have the composition generally approximating to R_2O, Al_2O_3, $6SiO_2$, in which R may be either potash or soda. It is probable that very few of the large deposits will run higher than 10 per cent. potash and in many the percentage of soda is considerable and presents a decided complication in any scheme of potash extraction.

When in a finely ground condition, orthoclase is not a difficult silicate to decompose and a number of methods have been proposed and successfully carried out on a small scale. None of these have, however, up to the present time developed into successful commercial operations. Water alone, to a slight extent, decomposes feldspar and will extract a small amount of potash from fine-ground orthoclase, but the action is not continuous and soon practically ceases, owing to the accumulation of the resulting decomposition products, which may form new combinations of a more or less insoluble nature and which also protect the active surface area of the particles from continued decomposition. If the insoluble products are removed by abrasion, solution, electrolysis, or other

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[1] *Bull.* **104,** *Bur. Plant Ind., U. S. Dept. Agr.*

[2] *Bull.* **28,** *Office Public Roads, U. S. Dept. Agr.*, p. 16.

means, the action goes further, but in any case the amount of decomposition depends upon the available surface offered by the powder and therefore upon its degree of fineness. This is true of any reaction which is purely a surface one and is a factor which, in many similar cases, deserves more consideration than is ordinarily given it. Some figures have been presented in a previous publication which show the enormous increase in surface area which results from reducing one pound of feldspar in the shape of a solid cube to the condition of the finest possible powder. It has been shown that whereas the original cube would have a surface area of 29.3 square inches, the same material reduced to particles just capable of passing a screen containing 200 meshes to the linear inch would have an area approximately equal to 24,900 square inches. If further reduced entirely to the finest possible powder, the surface area mounts into millions of square inches.[1]

In a previous publication on the decomposition of the feldspars the authors have already discussed to some extent the effect of fineness of grain on the rate of decomposition and have presented certain data in regard to an electrolytic method for extracting the soluble alkalies from ground rock.[2] Some results of a study of very fine powders have also been presented by the authors in a paper on the air elutriation of fine powders in which a laboratory method for separating the very finest powders from coarser particles was described and the relation of fineness to surface area discussed.[3] By means of an apparatus which may be briefly described as consisting of a series of settling chambers through which the powdered spar is forced by air pressure, a number of samples of the material were obtained differing considerably in the relative size of their particles. From microscopic measurements of the average diameter of the largest, smallest and medium-sized particles in each sample, and taking into account the relative proportion of each of these different sizes present, a close approximation was made of the actual surface area presented by a unit weight of powder, by means of the following formula where M_1, M_2, M_3 equal the per cent. of large, medium and small sized particles and l_1, l_2 and l_3 equal their respective diameters:

$$a = 6\left(\frac{M_1}{l_1} + \frac{M_2}{l_2} + \frac{M_3}{l_3}\right).$$

The object of this paper is to present the results of the continuation of these researches, together with a brief review of our own previous work and that of other investigators.

In our former work the decomposition of an impure orthoclase, as

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[1] *Bull.* 104, *loc. cit.*

[2] *Bull.* 28, *Office of Public Roads, U. S. Dept. Agr.*

[3] THIS JOURNAL, 29, 4.

procured in bulk from a commercial firm, was studied, no attempt being made, however, to obtain exact measurements of the fineness of the product, although it was found that nearly 98 per cent. would pass through a standard 200-mesh sieve. This material was found, by analysis, to have the following composition and was used in all of the experiments described in this paper:

Silica (SiO_2)	68.29
Alumina (Al_2O_3)	18.27
Potash (K_2O)	9.32
Soda (Na_2O)	3.60
Phosphoric anhydride (P_2O_5)	0.53
Total	100.01

When leached with water, the powder gave a yield of 0.025 per cent. alkalies in solution, although it was demonstrated that a greater amount had actually been produced by the action of the water and that the difference between this amount and that passing into solution had been combined with or absorbed by the insoluble substances also formed. Wet grinding in a ball mill, by which the particles were further broken down and the insoluble products removed by abrasion, produced a yield of 0.32 per cent. alkalies. It was found that the absorbed alkalies could be removed by electrolysis, and by this method the dry ground powder gave a yield of 0.14 per cent. alkalies while as high as 0.45 per cent. were extracted from the wet re-ground material. From fourteen re-grindings and electrolytic runs on the same sample it was found possible to extract 3.54 per cent. alkalies with water alone, which represents a decomposition of about 27 per cent. and indicates that total decomposition could be brought about by repeating the operation of regrinding and electrolysis a sufficient number of times. Because of the time and energy involved in this method, the results obtained are, of course, interesting from a theoretical point of view only.

The action of water can, of course, take place only upon the free surfaces of the particles, and as this surface is a function of fineness of grain it was decided to attempt the determination of the relative amount of alkalies which could be extracted by water from samples of different degrees of fineness. For this purpose some of the feldspar was obtained in massive form, crushed in an iron crusher and then passed through a set of standard mesh sieves. The powder retained between each consecutive pair of sieves was given a number, and its particles assigned the average diameter of the two meshes. For the coarse material this method was considered sufficiently accurate. Material which would pass through the 200-mesh sieve was separated by the air elutriation into three samples and microscopic measurements were made as previously described.

The area of a unit weight, or in this case, a unit volume (1 cc.), of solid material broken down to the sizes represented by the different samples was then calculated, from the formula previously given, for use in comparing the relative amount of the alkalies liberated. The results of these measurements are given in the following tables:

TABLE I.—COARSE POWDERS.

No.	Mesh.	Average diameter. mm.	Area per cc. sq. cm.
1	10– 20	1.3970	43
2	20– 30	0.7239	83
3	30– 40	0.4695	128
4	40– 50	0.3465	173
5	50– 80	0.2493	241
6	80–100	0.1605	374
7	100–200	0.0994	604

TABLE II.—FINE POWDERS.

No.	Diameters. mm.	Per cent.	mm.	Per cent.	mm.	Per cent.	Area per cc. sq. cm.
8	0.0122	8	0.0061	15	0.00090	77	53,202
9	0.0063	3	0.0025	10	0.00018	87	292,685
10	0.0037	3	0.0007	14	0.00010	83	510,486

In order that a number of electrolyses could be carried on at the same time and under the same conditions, a battery of six cells was constructed as shown in Fig. 1.

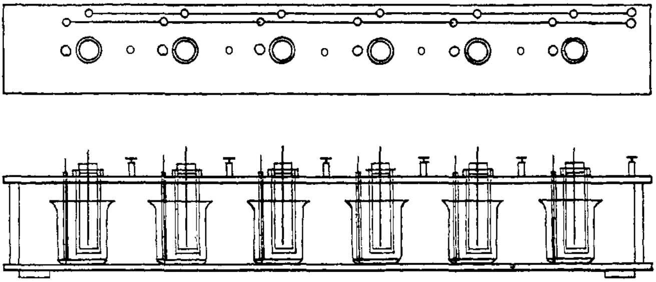

Fig. 1.—Arrangement of electrolytic cells.

Each of these cells consisted of a 400 cc. Jena glass beaker which served as cathode compartment and a cylindrical wooden pine cup 5 inches high—1.5 inches external diameter and 1/8 inch thick, for the anode or slime chamber, which also served as a porous diaphragm. An adjustable rubber collar placed around the tops of these cups allowed them to be hung in the rack above the beakers so that the bottom of each cup was about 0.5 inch from the bottom of the corresponding beaker. The anodes were made of heavy platinum wires which passed through stoppers fitted in the mouths of the wooden cups, and the cathode in each cell consisted of a layer of mercury covering the bottom of the beaker and connected to the binding post by means of a platinum wire running through a sealed glass tube. The binding posts were arranged in such a manner that the cells could be connected either in parallel or series. When run in parallel the anode and cathode wires were connected to the binding posts joined to the main line while a series connection could be made by means of the auxiliary binding posts placed between the cells in such a manner that the cathode of one could be connected to the anode of the next. The cups were first treated with alcohol to remove as much resin as possible and then well soaked in water. Blank runs were made upon each cup until no indication of alkalinity could be observed by the use of phenolphthalein in the cathode compartment.

Twenty grams each of the coarse samples were slimed in the anode chamber with 50 cc. distilled water and 200 cc. distilled water was placed in the cathode compartment. The cells were run in series on a 220-volt line. A number of 48-hour runs were carried on until practically no more alkalies were liberated, and titrations of the cathode liquor with N/10 HNO_3 made at the end of each run to determine the amount of $K_2O + Na_2O$ extracted. Each run was begun with fresh distilled water in the cathode compartment. Electrolyses of the fine powders were

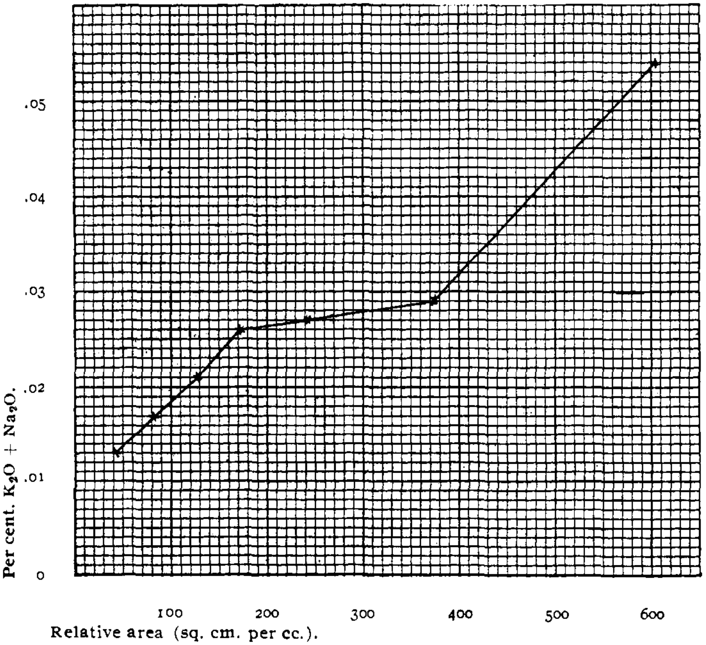

Fig. 2.—Electrolysis of orthoclase with water (coarse powders).

made in the same manner with the exception that, the supply being somewhat limited, 3 grams were used instead of 20. The results for both the coarse and fine powders are given below and are followed by diagrams (Figs. 2 and 3). It was found necessary to construct diagrams of different scale for the coarse and fine powders, as the relative areas exposed make it impossible to compare the different order of magnitudes on one scale.

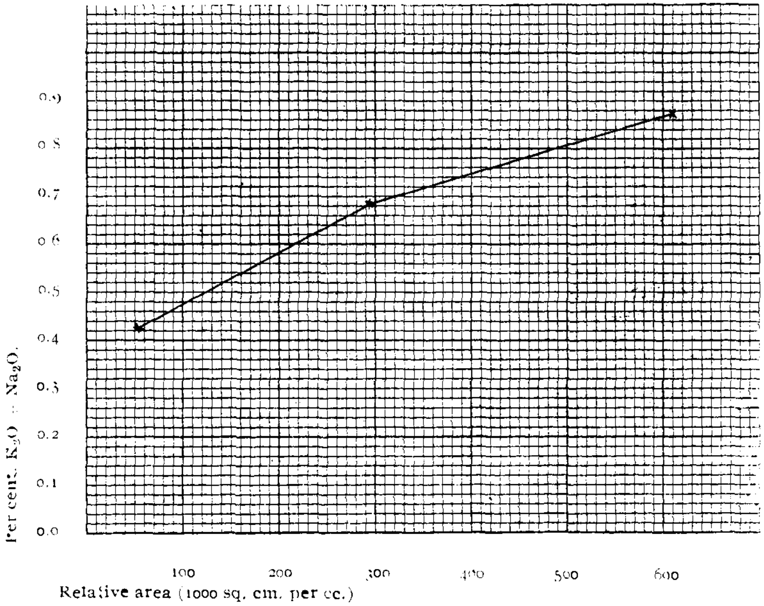

Fig. 3.—Electrolysis of orthoclase with water (fine powders).

TABLE III.—COARSE POWDERS.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.
Sq. cm. per cc......	43	83	128	173	241	374	604
Per cent. K_2O+Na_2O	0.013	0.017	0.021	0.026	0.027	0.029	0.054

TABLE IV.—FINE POWDERS.

	No. 8.	No. 9.	No. 10.
Sq. cm. per cc..................	53,202	292,685	510,486
Per cent. K_2O + Na_2O...........	0.423	0.683	0.873

Although these results plainly show an increased yield, the solution effect is not in exact ratio to the increase of surface area. It is probably true that as the particles decrease in size the tendency to clump and coagulate increases, and that, therefore, the theoretical surface area obtained does not entirely come into play. Although our investigations do not include a sufficient number of different sized powders to demonstrate this point, it is apparent, from theoretical considerations, that some reverse action must take place with increasing fineness. If this were not true, powdered orthoclase made up of ultimately fine particles should be rapidly and completely decomposed by water, which is not the case. This point will be discussed more fully later on, but it may be stated that this case is not essentially dissimilar to that of the gas law, which is subject to an increasing correction with increasing pressure until finally it no longer holds. It is not to be supposed that the decomposition of the feldspar is actually effected by the action of electrolysis, as the electric current merely transfers the soluble basic products of the hydrolysis. The simplest reaction which can be written to express the action of water on orthoclase is as follows:

$$KAlSi_3O_8 + HOH = HAlSi_3O_8 + KOH.$$

By a splitting off of silica from the hydrated aluminum silicate we can account for the formation of kaolin.

$$2HAlSi_3O_8 + H_2O = (H_2O)_2.Al_2O_3.(SiO_2)_2 + 4SiO_2.$$

It is certain, however, that the actual reactions which take place during the process of kaolinization in nature are more complex than these, and that intermediate zeolitic compounds of varying composition are formed in which water, if not potash itself, is held in the form of a solid solution.[1] It is difficult to determine whether similar intermediate products are formed when water acts on orthoclase powder under the conditions maintained in these experiments. It has been shown, however, that in whatever condition the potash is held in the decomposition products of orthoclase it is possible to extract it by electrolysis.

As feldspar is known to be partially decomposed by concentrated sulphuric acid, it was thought that a comparison of the decomposition of different sized powders could be readily obtained by this means. A series of digestions and determinations of alumina was accordingly made, and while the time exposed and relative proportions of powder and acid varied somewhat in the different experiments, as described under the respective tables, the method in general was as follows:

Weighed amounts of the powder were mixed with known volumes of H_2SO_4 (sp. gr. 1.84) and allowed to digest on the steam-bath for definite lengths of time. They were then diluted and filtered, and either the whole or an aliquot part of the clear filtrate was analyzed for alumina in the usual manner, by precipitation with NH_4OH. If the filtrate was cloudy, a sufficient amount of ammonia was added to cause the suspended particles to settle, but not enough to neutralize the acid and precipitate the alumina. An aliquot portion of the clear supernatant liquid was then analyzed.

The coarse powders were obtained in the same manner as described for the electrolysis, with H_2O, with the addition of thoroughly washing

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[1] *Z. anorg. Chem.*, 15, 318.

them on the sieves with a strong stream of water after they had been dry-sifted. They were then dried and all traces of iron from the crusher removed by means of an electro-magnet. Six grams of each sample were digested with 10 cc. of acid for eighteen hours, as described. Fig. 4 and its accompanying table give the results of these experiments.

TABLE V.—COARSE POWDERS.

Sq. cm. per cc.	43.	83.	241	604.
Per cent. Al_2O_3	0.041	0.078	0.098	0.160

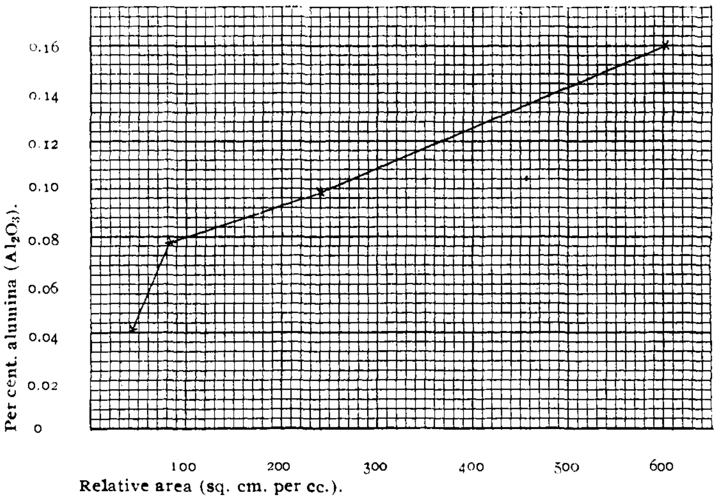

Fig. 4.—Solubility of orthoclase in sulphuric acid (coarse powders).

Four different experiments were made upon the air elutriated powders, the conditions and the results being given in the following table, made to accompany Fig. 5. Microscopic measurements and determinations of relative volume proportions were made in the same manner as described for the fine material in the electrolytic experiments. As the surface areas were also calculated in the same manner, it seems unnecessary to give the actual measurements here.

TABLE VI.

Symbol.	Conditions.		Chamber. 1.	Chamber. 2.	Chamber. 3.	Chamber. 4.	Chamber. 5.
⊙	3 gms., 24 hrs.	Per cent. Al_2O_3	0.333	0.747	....	....	2.007
	10 cc. H_2SO_4	sq. cm. per cc.	5,958	11,184	....	....	526,080
△	6 gms., 18 hrs.	Per cent. Al_2O_3	0.267	0.480	....	1.107	....
	10 cc. H_2SO_4	sq. cm. per cc.	5,958	11,184	....	95,160	....
⊡	6 gms., 96 hrs.	Per cent. Al_2O_3	0.313	0.643	1.090	....	....
	10 cc. H_2SO_4	sq. cm. per cc.	5,958	11,184	34,284	....	....
X	6 gms., 19 hrs.	Per cent. Al_2O_3	0.187	0.357	0.587	0.750	1.010
	10 cc H_2SO_4	sq. cm. per cc.	5,118	9,546	21,366	103,470	475,314

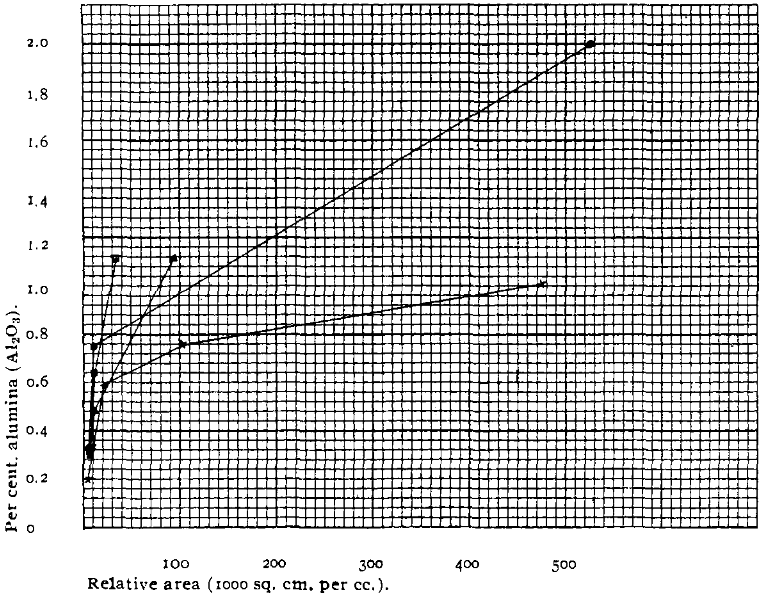

Fig. 5.—Solubility of orthoclase in sulphuric acid (fine powders).

In reviewing the diagrams for solubility with respect to area exposed, it will be seen that there is unquestionably a tendency toward greater solubility as the powder becomes finer, but here again in no case is the solubility shown to be directly proportional to the surface area. As these differences are in every case too great to be laid to the charge of experimental error in analysis, it was decided that it would be of interest to determine the solubility of some substance about which there could be no question in regard to surface area exposed to the action of a solvent. Sheet copper was selected as being the most homogeneous material readily obtainable, and pieces of known area, after being thoroughly cleaned, were subjected to the action of normal nitric acid for the same length of time in the same vessel, especial precautions being taken to keep the temperature as constant as possible and thus to avoid convection currents. The loss in weight of the samples was then determined and the results plotted as shown in Fig. 6.

A number of tests were made, in which the size of the test pieces and the concentrations of acid were varied, but in every case the curve representing any one series was more or less erratic in its direction.

It is certain that varying conditions play an important part in the relative solubility of different sized particles of the same material but within certain limits the solubility or decomposition effect rises rapidly with increasing fineness.

In previous work it was demonstrated that when powdered feldspar was slimed with water and a small amount of hydrofluoric acid and electrolyzed in the manner described for the water electrolyses, a far greater amount of decomposition took place than could be theoretically deduced from the action of the quantity of hydrofluoric acid present.[1] This result was due to the regeneration of the acid and in the run described it was found that 87 per cent. decomposition had been produced by the action of 20 cc. of 35 per cent. hydrofluoric acid upon 200 grams of the ground orthoclase. All of the bases, including alumina, were carried to the cathode compartment, the alumina being held mainly in solution as an alkaline aluminate, while silica alone is the final product left at the anode.

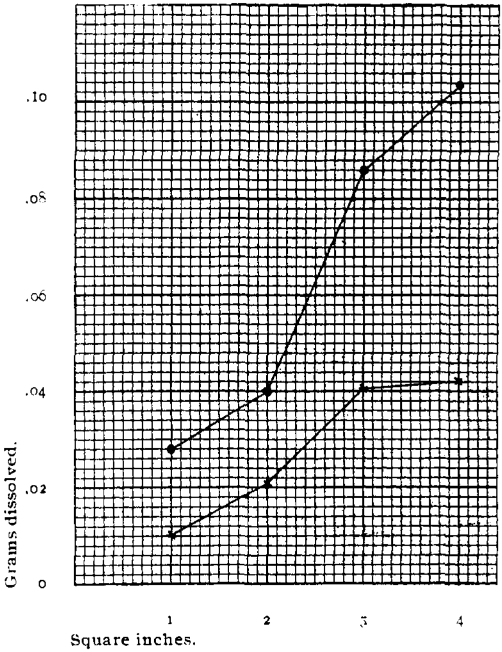

Fig. 6.—Solubility of copper in nitric acid.

The mechanism of these reactions would seem to be as follows: Taking, for the sake of convenience, an abbreviated form of the orthoclase molecule and considering the primary reaction when attacked by hydrofluoric acid, we may write the following equations:

1. $4KAlSi_3O_8 + 64HF = 4KF + 4AlF_3 + 12SiF_4 + 32H_2O$.

If potassium fluoride is added to a solution of aluminum fluoride, a difficultly soluble double salt is formed, and so we should expect the following reaction:[2]

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[1] *Bull.* 28, *Office Public Road*, *U. S. Dept. Agr.*

[2] Dammer's Anorg. Chem., III, 97.

$$2.\ AlF_3 + 4KF = AlF_3.4KF.$$

This slightly soluble double salt is slowly hydrolyzed, the potash and alumina being carried to the cathode chamber while the hydrofluoric acid is set free at the anode to immediately attack fresh orthoclase particles.

The silicon tetrafluoride is changed to hydrofluosilicic acid and silicic acid according to:

$$3.\ 12SiF_4 + 16H_2O = 4Si(OH)_4 + 8H_2SiF_6.$$

Finally it appears that the hydrofluosilicic acid is again broken up by hydrolysis according to:

$$4.\ H_2SiF_6 + 4H_2O = 6HF + Si(OH)_4.$$

It has been shown that only about one-tenth of the amount of hydrofluoric acid necessary to complete the reaction, according to the stoichiometrical relations involved, suffices to bring about complete decomposition of the orthoclase. This can only be explained by supposing that some such reactions as are given above take place.

The next problem was to study the effect of fineness of grinding on the rate of decomposition. No relation between the amount of decomposition with respect to area exposed can be determined unless the reaction proceeds to a finish and as, in the electrolysis of orthoclase with hydrofluoric acid, this point is reached only when decomposition is complete, it is evident that a comparison between these two factors is impossible by this means. The effect of fineness upon the time necessary for complete decomposition under the same conditions can, however, be determined, and with this object in view electrolyses with hydrofluoric acid were made on the three fine powders described as Nos. 8, 9 and 10 in the water electrolyses. One cubic centimeter of hydrofluoric acid was added to each of the anode liquors and the runs continued as before, with the exception that the cells were connected in parallel instead of in series. The length of these runs was the same for all of the cells in each particular case, but the amount of current flowing varied somewhat, of course, with the individual cells. In the sixth run another cubic centimeter of acid was added in order to hasten the operation. The cathode liquors were carefully titrated with standard acid after each run, and the results obtained are given in the following table:

TABLE VII.

Run.		Time. Hours.	No. 8. cc.	No. 9. cc.	No. 10. cc.
	With water alone..............		2.70	4.35	5.55
1	with H F.....................	48	6.45	8.55	13.65
2	" "	24	8.55	9.65	11.20
3	" "	24	7.70	9.00	11.15
4	" "	24	5.00	5.35	7.35
5	" "	24	0.30	2.20	2.80

TABLE VII (*Continued*).

Run.			Time. Hours.	No. 8. cc.	No. 9. cc.	No. 10. cc.
6	"	"	24	5.40	10.80	18.20
7	"	"	24	2.00	6.40	6.15
8	"	"	24	2.20	8.95	6.10
9	"	"	24	5.45	11.25	1.95
10	"	"	48	9.65	5.20	0.15
11	"	"	24	8.85	0.50	0.00
12	"	"	24	8.70	0.30	
13	"	"	24	5.15	0.00	
14	"	"	24	2.70		
15	"	"	24	2.40		
16	"	"	24	1.50		
17	"	"	24	0.10		
18	"	"	24	0.00		
Total cc.				84.80	82.50	84.25
No. of hours				456	336	288

It will be noticed that the reaction was completed with the finest powder first, the next finest second, and the coarsest third.

The actual amounts of alkalies set free as shown by the total titrations are given in the following table. In order to calculate the per cent. decomposition which this represents, it was found necessary to determine the quantity of alkalies present in the three classes of material obtained from the air elutriator, as the relative amount of quartz present in the samples varied with the different sizes, owing to its greater hardness and consequent lack of fineness. All of these results are given below:

TABLE VIII.

	No. 8.	No. 9.	No. 10.
Alkalies liberated from 3 gms.	0.3998 gm.	0.3890 gm.	0.3972 gm.
Per cent. alkalies liberated	13.33%	12.97%	13.24%
Per cent. alkalies contained	13.29%	13.63%	13.74%
Calculated per cent. decomposition	100.00%	95.16%	96.36%

To check this work very roughly, an analysis was made of the residue obtained from the electrolysis of sample No. 3. It was found to contain silica and alumina in the following proportions:

	Per cent.
SiO_2	98.80
Al_2O_3+	1.13
Total	99.93

It would seem, therefore, that all of the alkalies had been liberated instead of 96.36 per cent., as represented in the preceding table. The low results obtained on samples 9 and 10 by titration are undoubtedly due to a slight diffusion of the hydrofluoric acid through the wooden cups to the cathode compartment. The reason for the fact that some alumina was present in the residue is explained by the low solution pressure of aluminum fluoride, which allowed the more soluble alkaline fluorides to be transported first. It was noticed that as the yield of alkalies decreased alumina came over in greater amounts, and this transfer would have undoubtedly been complete had electrolysis been carried further.

Assuming, therefore, that decomposition in each of the three cases was complete, the approximate effect of surface area upon time necessary to bring about this decomposition can be shown as in Fig. 7, when the ordinates represent the time covered by the total number of runs and the abscissas the surface area presented.

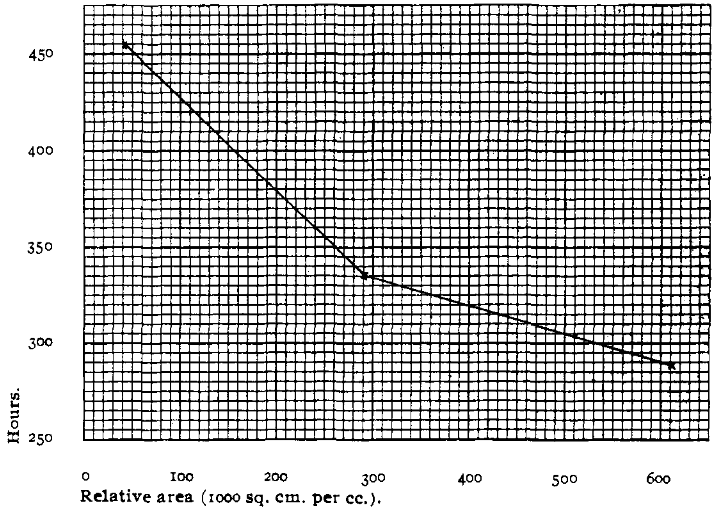

Fig. 7.—Electrolysis of orthoclase with hydrofluoric acid (fine powders).

In reviewing the diagrams showing the effect of fineness upon the extent of decomposition with water, as well as upon the time required to bring about complete decomposition with hydrofluoric acid, it will be noted that while the results do not strictly conform to theory, important differences in the reacting power of the different sized powders are shown to exist. The same remarks which were made upon the experiments with sulphuric acid are applicable here, and while it is true that a number of factors which it is impossible to take into account have a very important bearing upon work of this nature, it is nevertheless evident that in the extraction of potash from feldspathic rocks or, in fact, in any process of a similar nature, the effect of surface area of fineness of the material is a factor which deserves serious consideration. The slight solubility of the double fluorides of aluminum and potassium is one cause of the slowness of the separation of the bases in the electrolytic process, but it is possible that this difficulty might be overcome if the work were being conducted upon a large scale. Even if these difficulties did not exist, however, the prevailing price of potash and high cost of electrical energy would probably be a bar to the electrolytic process.

A study of the decomposition of the feldspars could not be considered complete unless it included all the methods of attack which have been proposed by others, or which have suggested themselves to the writers. The analytical method of J. Lawrence Smith, for decomposing silicates, has very naturally been made the basis of a number of processes, on some of which patents have been granted in various countries. Patents for fusion methods with salt or lime, or both, in combination, were granted in England to Tilghman 1847, Newton 1856, and Ward 1857.[1] In 1882 Spiller proposed a method for making potash alum from feldspars, which depended upon treating a mixture of the ground minerals with sulphuric acid. Pemberton showed later that this method could not possibly produce alum for a sufficiently low cost to justify its use.[2] More recently, Rhodin's process of fritting at 900°, a mixture of 100 parts of ground feldspar with 53 parts of quicklime and 40 parts of salt, has been to some extent exploited in England and in Sweden.[3] By this process it is claimed that about 90 per cent. of the potash present is converted into chloride and can be easily leached from the frit. It is possible that this mixture could be burned in continuous rotary kilns operated in a similar manner to those in use in cement manufacture. The fact, however, that the salt and lime combine with the silica and alumina to make a by-product of little or no value has undoubtedly prevented the development of this method into a commercial process. Lake has lately obtained an English patent[4] for treating leucite with sodium hydroxide or carbonate and quicklime. The inventor writes the following reactions in describing his process:

1. $Al_2O_3.K_2O.4SiO_2 + 4NaOH + 3CaO = Na_2O.3CaO.4SiO_2 + Al_2O_3.Na_2O + K_2O + 2H_2O;$
2. $Al_2O_3.K_2O.4SiO_2 + 2Na_2CO_3 + 3Ca(OH)_2 = Na_2O.3CaO.4SiO_2 + Al_2O_3.Na_2O + K_2O + 2CO_2 + 3H_2O.$

Although complete decomposition undoubtedly takes place by this method, the above reactions are open to criticism. There is no apparent reason why the soda should all enter into combination, leaving potash in a free state. Blackmore[5] has been granted a patent for the separation of alkali salts from insoluble combinations by treat-

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[1] *J. Soc. Chem. Ind.*, **20**, 5, 440.

[2] *Chem. News*, **47**, 1206, 5.

[3] *J. Soc. Chem. Ind.*, **20**, 5, 438.

[4] *English Pat.*, 17,985.

[5] *U. S. Patent*, 772,206 (1904).

ment with carbonic acid under high pressure. The writers have had no experience with this method, but it is doubtful whether, even if it is successful chemically, it could be developed into a commercial process.

The writers have found that fusion or fritting with calcium chloride will decompose feldspar but here again, even under the most favorable circumstances, it is unlikely that such a method of attack could be made economical.

Sodium nitrate and mixtures of sodium carbonate and nitrate decompose feldspars at comparatively low temperature. As sodium nitrate is extensively used as a fertilizer, and as it may possibly be eventually manufactured in part from atmospheric nitrogen, it is at least interesting to note in passing that it is possible to enrich it with soluble potash by fusion with ground feldspar and regrinding.

It will be seen, however, that the weak point in all the methods of attack so far discussed is the unavoidable formation of large quantities of by-products which, though made from more or less costly raw materials, are of no value in the end. This difficulty can apparently only be overcome by the use of potash compounds to attack the feldspar, since the potash used is at least as valuable after the process is completed as it was before. The writers have tried a number of methods of attack with various compounds of potash. Some of these experiments have led to interesting results which may possibly be found to have a bearing upon the practical problems of potash extraction. If fine-ground orthoclase is mixed with potassium carbonate or hydroxide and heated at a dull red heat for a short time, the decomposition of the feldspar takes place rapidly. The decomposition becomes complete when the orthoclase and potassium carbonate are present in the ratio of 1 : 1.6 parts. On taking up with hot water a white flocculent precipitate of definite composition is formed which is readily soluble in dilute acid. On careful analysis of this white precipitate, made from different samples of orthoclase, it appears to be the potassium analogue of natrolite, the well-known sodium aluminum orthosilicate, the formula of which is

$$(H_2O)_2K_2OAl_2O_3(SiO_2)_3.$$

Fusions were made of two different orthoclases in the following manner:

One-half gram of the powdered orthoclase was ground with 0.8 gram of potassium carbonate, the mixture transferred to a platinum crucible and heated to a dull red for 15 minutes. When cool, the fusion was taken up with hot water, digested on a steam-bath for five minutes in order to obtain a flocculent precipitate, and filtered, the precipitate being washed with boiling water until the last washings were neutral to litmus. The precipitate or synthetic silicate was then dissolved in hydrochloric acid and analyzed in the ordinary manner. The following table gives the results obtained, calculated in per cent. of the original powder taken:

TABLE IX.

	Theoretical orthoclase.	Orthoclase. A.	Synthetic silicate from A.		Orthoclase. B.	Synthetic silicate from B.	
			1.	2.		1.	2.
SiO_2	64.84	68.29	33.68	33.80	66.52	32.78	32.78
Al_2O_3	18.29	18.27	18.36	18.24	18.32	18.32	18.26
P_2O_5	...	0.53	0.15	0.16	...	...	...
K_2O	16.87	9.32	16.28	16.39	13.53	17.54	17.36
Na_2O	...	3.60	1.19	1.16	1.63	...	...
	100.00	100.01	69.66	69.75	100.00	68.64	68.40

Using the data given above, the percentage composition of these precipitates can be calculated, showing the probable synthesis of a potash analogue of natrolite. The percentage composition of an anhydrous potash form of natrolite is also given for the sake of comparison.

	Composition of anhydrous potash form of natrolite.	Composition of anhydrous residue from orthoclase A.	Composition of anhydrous residue from orthoclase B.
SiO_2	47.97	48.51	47.84
Al_2O_3	27.06	26.32	26.69
K_2O	24.97	25.17	25.47
	100.00	100.00	100.00

The above results can best be interpreted by the following reactions:

1. Reaction during fusion.

$$K_2O . Al_2O_3(SiO_2)_6 + 6K_2CO_3 = 6K_2SiO_3 + K_2Al_2O_4 + 6CO_2.$$

2. Reaction of fusion with water:

$$6K_2SiO_3 + K_2Al_2O_4 + 5H_2O = (H_2O)_2 . K_2O . Al_2O_3(SiO_2)_3 + 6KOH + 3K_2SiO_3.$$

Leaving aside the question of whether or not such a method of attack could be considered from a commercial standpoint, it is none the less apparent that complete decomposition of the feldspar takes place, with a synthesis of a silicate rich in potash which would be easily made available in the soil or for further extraction treatment in the factory.

The latest process for the extraction of potash from feldspar which has been granted a patent in the United States is that of Swayze,[1] which takes advantage of the principle of the potash attack upon the silicate. According to the specifications for this process, coarsely ground feldspar is first heated to partially destroy its crystalline structure, and it is then heated under pressure with a strong solution of caustic potash. By subsequent chemical treatment it is proposed to manufacture potash, alum and fine silica as the end products of the various operations. Although it is doubtless true that orthoclase can be largely decomposed by this method, the reactions involved are necessarily similar to the fusion methods just described with subsequent treatment with water, and it is doubt-

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[1] *U. S. Patent*, 862,676 (1907).

ful whether the necessary separations of the products could be profitably made.

Another method which has suggested itself, as a result of the writers' investigations, is treatment of the ground orthoclase with a certain proportion of hydrofluoric acid, taking advantage of the reactions given on pages 790–1, but without the subsequent electrolysis. By filtering cold on a cloth filter, nearly all of the potash present is held in the residue in the form of a double fluoride with alumina. By subsequent heating with ground limestone or lime, the potash is readily made soluble, and, if it is desired, can be leached out. Unfortunately, the excess of lime present makes it impossible to recover the hydrofluoric acid.

It would seem probable that some one of these methods which have been described or suggested, could be developed under favorable circumstances into a successful commercial process. The above data are presented in the hope that it will stimulate experimentation on a larger scale than is possible in a chemical laboratory and result in a successful solution of an important industrial problem.

The results given in this paper may be summarized as follows:

(1) Fine grinding of feldspars renders the potash partly available under the action of water. The addition of certain substances, such as ammonium salts, lime and gypsum, increases this effect.

(2) It is possible to completely extract potash by an electrolytic method either with or without the addition of hydrofluoric acid, but it is probable that this method could not be used commercially on account of its cost.

(3) The effect of fineness of grinding has been studied and data given showing the relation of surface area to rate of decomposition.

(4) It is shown that there are numerous fusion methods which could be used successfully if the cost were not too high. The attack on the silicates by means of potash or its compounds yields some interesting reaction products which might possibly be made use of.

(5) The attack with hydrofluoric acid is suggested as a possible method that deserves further study.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

FLASK FOR FAT DETERMINATION.

W. L. DUBOIS.

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The Knorr apparatus for the extraction of fat employs a flask which is fragile, very difficult to clean and expensive to replace. A number of attempts have been made to supplant these flasks with simpler ones