

A STUDY OF THE EXTRACTION OF POTASH FROM ORTHOCLASE
FELDSPAR BY CARBON DIOXIDE AND SULPHUR DIOXIDE.
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the Faculty of Dalhousie College for the Degree of Master
of Arts, March 19, 1921.

(Read 9 May, 1921)

Introduction.—The term potash usually includes any simple compound of potassium from which the metal or any particular salt can be easily obtained. Such deposits of potash are of remarkably rare occurrence, insomuch that the world has been dependent on one or two sources for almost its entire supply of this indispensable substance.

The largest deposit, and the one which has supplied practically all demands since 1860, is that in Northern Germany known as the Stassfurt Deposit. The next largest bed of potassium salts is in Alsace, and the fact that this country has recently changed ownership will introduce an element of competition in the potash trade. Another large deposit has been found in Spain, and smaller deposits in Galicia and California, while a certain percentage of these salts is obtained from the nitre beds of Chili, and a further small quantity is recovered from a few industries, as cement mills, molasses distillery slop, and beet-sugar refineries.

But while potassium in suitable form occurs only in a few places, yet it is widely distributed as a component of rocks and soil, and is also found in vegetable and animal substances. In 1914 the supply of potassium salts from Germany was cut off, and it became necessary to discover some other source from which to obtain the potash required by the industries. As orthoclase is a mineral of very common occurrence, and in unlimited quantity, and contains from 9% to 14% K_2O , a great deal of research work has been done on it in the endeavor to extract its potash content.

Historical.—Though it was during the period of the Great War that attention was more particularly focussed on feldspar as a possible source of potash, yet attempts have been made to extract it from orthoclase since the middle of the 19th century. Patents for the recovery of the potash content of feldspars have been issued in the United States, Canada, and Great Britain

from 1854 to the present time. Quite a variety of methods are indicated. The greatest number of these involve the fusion process with a basic compound, usually one of the alkalis or alkaline earths. Others follow a process of digestion of the finely ground mineral with the same basic compounds, the time factor extending from a day to a month. Electrolysis of the moistened powder has also been tried but complete extraction is only arrived at after many repetitions of the treatment. Others have endeavored to solve the problem by heating the mineral in a finely ground state to a high temperature and suddenly cooling to destroy its crystalline nature, and then treating with an alkali under pressure. Another method is to treat the pulverized mineral with hydrofluoric acid and treat the residue with gypsum.

A few abstracts of patents issued will give a more definite idea of what has been done:

Cushman, U. S. Pat. No. 851922, 1907, mixed powdered felspar with water to form a thin sludge. This sludge was then placed in a wooden container which was set inside another larger vessel in which water was then placed. Electrodes are introduced, the positive pole being in the inner vessel and the negative in the outer. On the passage of a current, the potash, soda, and other soluble bases are partially liberated and pass into the water of the outer vessel. By agitating the sludge, or adding thereto a small amount of hydrofluoric acid, an almost complete recovery of potash is effected.

Messerschmitt, U. S. Pat. No. 1,076,508, 1913, extracts the potash from potash-bearing minerals, such as felspar, by powdering the mineral and forming a mixture of 1000 pounds of spar, 600 lbs. of basic calcium nitrate, 120 gallons of water, and 200 lbs. of lime. This mixture is introduced into a digester and heated under pressure of 50-125 pounds for 10-24 hours. The sludge obtained is leached with water and a solution of potassium nitrate is obtained. Any calcium nitrate present is thrown down by the addition of an alkali carbonate to the solution and filtered out. The final solution is then evaporated.

Coolbaugh and Quinney, U. S. Pat. No. 1,125,007, 1915, mix felspar with gypsum or limestone, heat to fusion point, cool rapidly and crush to fine powder. This powder is then leached with water containing a small percentage of sulphuric acid, and

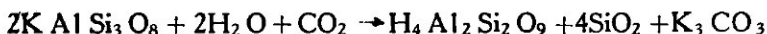
the potassium aluminum sulphates obtained in solution are separated by crystallization. A recovery of 90-92 per cent. of the potash contained in the felspar is claimed.

It is claimed that most of these methods give satisfactory results, but the cost of extraction is too great to permit of competition with the industries of Europe.

The future then of the potash industry on the American Continent, depends on the discovery and development of an economical process of separation.

Method.—In a foregoing paragraph several methods for decomposing felspar are outlined, but the decisive objection to these is their cost of operation. A cheap method is still being sought. Rocks are being decomposed continuously in nature in the general process of change and denudation. Statements of geologists on this matter will be of interest. The Encyclopedia Britannica says "It has been supposed that the alteration of the granite or felspar has been effected mainly by meteoric agencies, the carbonic acid having decomposed the alkaline silicate of the felspar, whilst the aluminous silicate assumes a hydrated condition and forms kaolin." It may be mentioned that the formation of kaolin and of potash is brought about by the same operation.

With regard to kaolinization A. W. Graham says:—"The ordinary effect of the atmospheric moisture on the rocks is the attack upon the felspars producing kaolin or clay. This commonly takes place in the presence of CO_2 . The formula for the alteration of orthoclase felspar into kaolin, quartz, and potash being



Bulletin 695, U. S. Geological Survey states, in effect, that felspathic decay is not formed by ordinary weathering but by the operation of thermal waters and gaseous emanations, and carbonated waters. While all these processes and others are operative yet the chief chemical activity is due to carbonic acid.

The most important gaseous emanation referred to is probably SO_2 . There is a deposit of potash in Hungary supposed to have been derived from orthoclase by the action of sulphurous emanations of a neighboring volcano.

Though nature works by means of these simple agents yet progress is very slow. Many chemical reactions can be hastened

by catalytic agents, and this is what has been attempted in the present case. (It will be remembered that the function of a catalyst is to increase the speed of a chemical reaction). Heat and pressure were employed. Platinum sponge was also given a trial.

Apparatus.—The first experiments were made with an ordinary Kipp carbon dioxide generator. A continuous stream of gas was passed through a water mixture of the finely ground felspar, heat and agitation being furnished by boiling. These experiments were, of course, carried out under atmospheric pressure only.

In order to conduct the work at higher pressures a special piece of apparatus was obtained. It was essentially a heavy iron retort consisting of a body of $3\frac{1}{2}$ " steel piping of $\frac{1}{4}$ " thickness. A piece of pipe $13\frac{1}{2}$ " long was taken and the ends closed by screwing on two heavy caps. A head 3" in diameter was cut out of one cap and into this removable head were screwed a pet-cock and an inlet pipe, both $\frac{1}{2}$ ". The head was held in place by a heavy clamp, and the inlet which extended to within an inch of the bottom of the retort was connected with the gas supply by means of a $\frac{3}{4}$ " junction. A hole was tapped in the side of the retort for the pressure gauge.

The gas and pressure were supplied by a cylinder of liquid carbon dioxide, the pressure was also furnished by superheated steam by the simple expedient of boiling with all valves closed.

The only other piece of apparatus used was a hand spectroscope with which qualitative tests were made for potassium.

Analysis.—A quantity of orthoclase sufficient for the work in hand was procured from the geological laboratory and an analysis made of it. The following results were obtained.

Silica,	SiO ₂	65.520%
Alumina,	Al O ₃	21.520 "
Potash,	K ₂ O.....	11.860 "
Soda,	Na ₂ O.....	1.675 "
Lime,	Ca O.....	.151 "
Magnesia,	Mg O004 "
		100.730%

In making a determination of potassium both the chlorplatinate and the newer perchlorate methods were followed. All things considered the results showed fair agreement. The only reagent it was necessary to prepare was the chlorplatinic acid. This was made by dissolving some scrap platinum in aqua regia. From time to time small amounts of concentrated hydrochloric acid were added but the platinum went into solution very slowly. The digestion required two or three days.

Experimental Results.—Two series of experiments were carried on, one with carbon dioxide, the other with sulphur dioxide. Considerable difficulty was met with from the presence of iron. Efforts were made to meet this nuisance by lining the retort with smoke-stack varnish, which helped in some degree but introduced more or less organic matter. In working out the determination the iron was removed by ammonia, which made it necessary to determine the potash as a chloride after removing the ammonium salts by ignition, while the organic matter was removed partly by filtering and partly by ignition. This made the process of determination rather long. The following is a table of results. The amount of K_2O shown is the percentage of the orthoclase, not of its potash content. The latter figure may be obtained, approximately, by removing the decimal point one place to the right.

Weight of Sample (grams)	Treatment	Time	Result	Remarks
8.3908	Heat & agitation (boiling)	2½ hrs.	Unchanged	
1.5212	" " " "	4 "	" "	Traces of iron
16.1080	CO ₂ & steam, atmos. press.	6 "	.158% K ₂ O	
13.2200	CO ₂ & intermittent boiling, "	4 "	.196% "	Little Iron
12.5794	CO ₂ no heat, pressure advanced	2 "	.161% "	Little Iron
15.4311	CO ₂ Interm't boiling, " "	2½ "	.458% "	Little Iron
60.5300	" no heat, Pressure 50 lbs.	2 "	.090% K ₂ O	
52.3200	" " " " " "	5 "	none	
28.6770	" intermittent heating by steam, pressure 100 lbs.	10 "	.145% K ₂ O	More iron
19.7476	CO ₂ sintered feldspar for ¾ hrs superheated steam, 100 lbs.	5 "	.224% K ₂ O	
2.3964	SO ₂ and boiling	1 hr.	.376% K ₂ O	residue dark
2.6800	" " "	2 hrs.	.396 "	" "
3.2020	" " "	4 "	.385 "	" "
15.0214	" " "	4 "	.334 "	" "
21.0526	SO ₂ sintered feldspar superheated steam, 100 lbs. press.	2 "	.300 "	" "

Successive Treatment with CO ₂					Time	Potash
Treatment	CO ₂	and Boiling,	Atmos. Press.,		2 hrs.	.132%
"	"	"	"	"	"	.100%
"	"	"	"	"	"	.115%

Certain deductions from these results are quite clear, while others remain problematical.

It seems that heat and agitation alone do not cause a measurable amount of decomposition, at least during a period of a few hours.

Considering the action of carbon dioxide it would appear at first that the time factor, heat, and agitation make practically no difference, the percentage of potash obtained being the same with a variation of these agents.

But when the preliminary experiment was made with a higher pressure and intermittent boiling an increase of decomposition was obtained, which suggested heat and pressure as being of some importance. Accordingly the special piece of apparatus previously described was procured, but the results were disappointing. It is obvious that the pressure used had no effect, and it was only when heat and agitation were employed that the degree of disintegration was brought up to what might be termed the normal amount.

It was thought that if the felspar were sintered the crystalline character of the mineral would be sufficiently destroyed to permit of more decomposition. This was accordingly done, but practically no change in the result was obtained.

The idea was gradually being acquired that the sample of orthoclase had previously undergone a certain degree of weathering or alteration of some kind in consequence of which a small percentage of the sample was subject to the action of carbon dioxide while the rest was unaffected. To test this idea a series of successive treatments was carried out. The sample was treated for two hours at atmospheric pressure with heat and agitation (boiling) and a continuous stream of carbon dioxide. The residue was reground and the treatment repeated. Practically the same amount of decomposition was obtained each time. This dispels the idea of prealteration and points to the conclusion that the breaking down of the felspar is of a progressive nature. It may be mentioned here that on filtering the reaction product a very fine clay light brown in color was always left on the filter. The reason for its color is not apparent,

but its presence confirms the fact of decomposition. After arriving at this conclusion of progressive decomposition it is interesting to recall Grünwald's experiments on the decomposition of feldspar by electrolysis. After fourteen repetitions he obtained about one-third the total potash content, and claimed to obtain complete decomposition by continuing the process.

With regard to the action of sulphur dioxide the same conclusion may be drawn, with this difference—that the percentage decomposition by this agent is much greater.

When platinum sponge was added to the reaction mixture no additional change was observed.

In summary, then, it is concluded: First, SO_2 is more effective than CO_2 in decomposing feldspar.

Second, Heat and agitation have a small value in combination with an active chemical agent.

Third, Platinum as a catalyst is of no value in this reaction.

Fourth, the value of the time factor beyond two or three hours is nil.

Fifth, The decomposition of feldspar is of the nature of an incomplete chemical reaction, the point of equilibrium being definite and appreciably different in the cases of SO_2 and CO_2 .

This is readily explained by the ionic hypothesis. Sulphurous acid is a weak acid and carbonic acid is very weak; consequently the degree of ionization is very small. The formation of a very small amount of the largely ionized salts of these acids is sufficient to repress the ionization of the acids, thus bringing about a state of equilibrium at a very early stage. This also explains why the time and pressure factors are of practically no value while the products of the reaction remain in the reaction mixture.

Sixth, As a process for extracting potash from orthoclase feldspar, this method is valueless.