

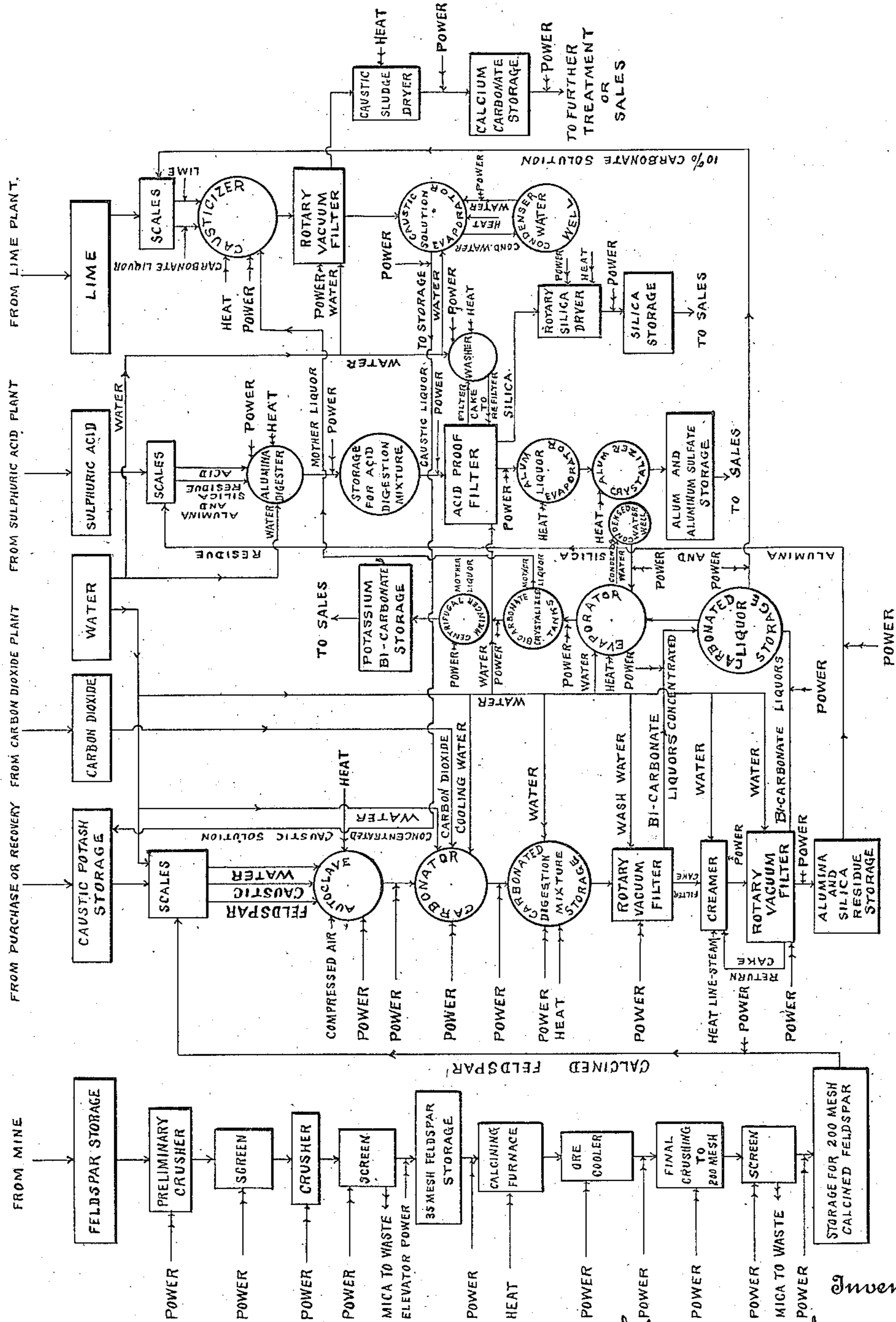
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S. W. SCOFIELD ET AL

PROCESS OF SEPARATING THE CONSTITUENTS OF MINERAL SILICATES

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Inventors

Sherran W. Scofield
and John B. Larue
George W. Samuel
 Attorneys

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UNITED STATES PATENT OFFICE.

SHERMAN W. SCOFIELD AND JOHN B. LA RUE, OF CLEVELAND, OHIO; SAID LA RUE
ASSIGNOR TO SAID SCOFIELD.

PROCESS OF SEPARATING THE CONSTITUENTS OF MINERAL SILICATES.

Application filed May 17, 1922. Serial No. 561,704.

To all whom it may concern:

Be it known that we, SHERMAN W. SCOFIELD and JOHN B. LA RUE, citizens of the United States, residents of Cleveland, county of Cuyahoga, and State of Ohio, have invented new and useful Improvements in Processes of Separating the Constituents of Mineral Silicates, of which the following is a specification, the principle of the invention being herein explained and the best mode in which we have contemplated applying that principle, so as to distinguish it from other inventions.

Our invention relates to processes for separating the constituents of mineral silicates, and particularly to processes for extracting the potassium and other values from potash feldspar. This invention relates to improvements in a process of this general character disclosed in our pending application for U. S. Letters Patent, Serial No. 407,724.

The annexed drawing and the following description set forth in detail certain steps embodying our invention, the disclosed steps, however, constituting but one of the various methods in which the principle of the said invention may be carried out.

The drawing represents a flow diagram of our improved process.

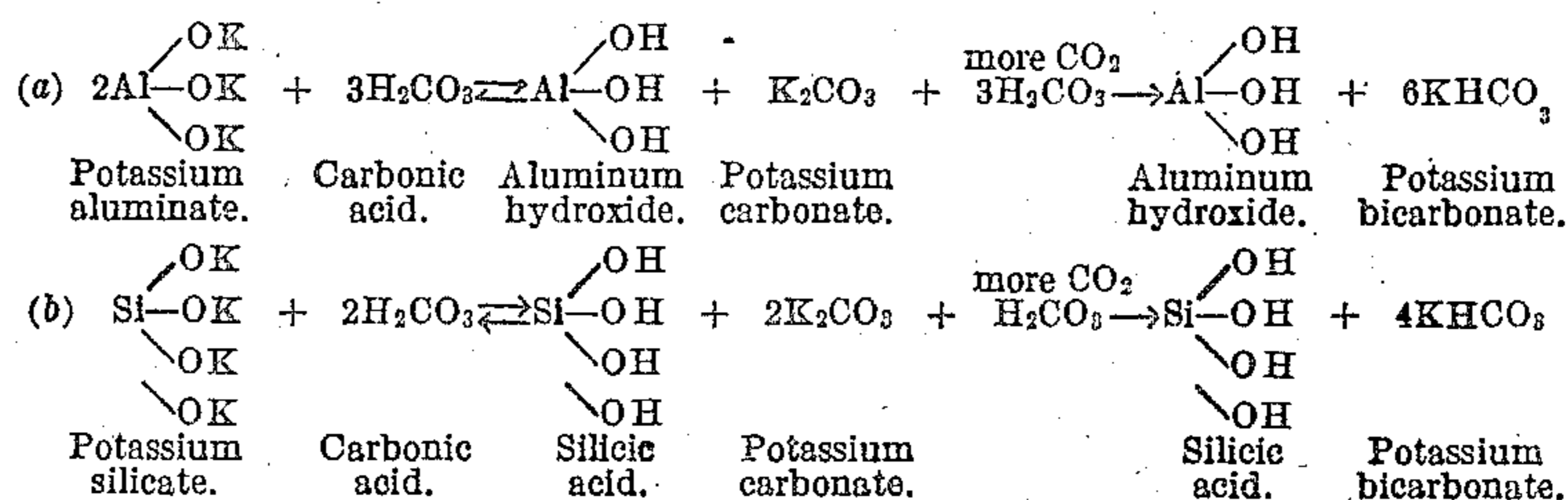
We first crush high grade crystalline potash-feldspar to about thirty-five (35) mesh, in order that a subsequent calcining can be thoroughly and economically effected. We then calcine this crushed ore until the same is converted to an amorphous condition, in order that a subsequent digestion with caustic potash may be effected to convert the ore constituents into water soluble or acid soluble compounds. This calcining is effected upon the bed of a furnace or in any other suitable manner by heating from one (1) to two (2) hours at from 800° to 1050° C. After the ore has thus been reduced to an amorphous condition, we then further crush the same to about two hundred (200) mesh after which the same is digested with the caustic potash. The digestion of the ore with caustic potash is not carried to a point where all of the ore is converted into water soluble potassium silicate and potassium aluminate but there is also produced a water insoluble but an acid soluble potassium aluminum silicate. We

use 90% caustic potash for the alkali digestion in amount from one and one-quarter (1 $\frac{1}{4}$) to two (2) times the weight of the ore, and also an equal amount of water, heating for from one (1) to two hours at a temperature from 275° to 325° C. The operation is effected in an autoclave at a pressure of from 300 to 350 lbs. per square inch. We then allow a further reaction period of about two (2) hours, resulting in a complete decomposition of the ore into the water or acid soluble compounds above-mentioned. During the digestion operation considerable hydrogen is formed, after the temperature has reached substantially 200° C., due to the fact that the iron walls of the autoclave are attacked by the strong caustic potash, the reaction being $Fe + 2KOH = Fe(OK)_2 + H_2$. It may be that some impurity in the ore or even in the iron acts as a catalyst for this reaction. The iron later appears as an impurity in the aluminum salts or possibly in the silica. In order that this evolved hydrogen may not form an explosive mixture with the oxygen of the air which is in the autoclave at the start, we remove this air from the autoclave during the first part of the digestion operation by allowing the pressure to reach thirty (30) to forty (40) lbs. per square inch and then allowing the oxygen to escape from the autoclave. The already formed steam displaces the air which escapes and finally the interior of the autoclave contains nothing but steam, indicated by a current of pure quickly condensing steam escaping from the autoclave valve.

We dilute the alkali digestion products with from one (1) to four (4) times their volume of water and then carbonate the mixture with carbon dioxide, maintaining a pressure of about 22 inches above atmospheric pressure, the temperature being maintained at substantially room temperature by means of a positive removal of the generated heat. We thus obtain the water soluble potash value in solution and precipitate aluminum hydroxide and ortho silicic acid. The mass action resulting from the pressure above-mentioned and the maintenance of normal temperature effects the carbonating in about forty-five (45) minutes, the same taking place in two stages, the first stage resulting in a conversion of the potassium content to potassium carbonate and taking

only about five minutes and the second stage converting the potassium carbonate to bicarbonate and taking about forty (40) minutes. The reaction is based upon the action of the ionized acid (H_2CO_3) formed by the dissolving of CO_2 gas in water. There is only incomplete precipitation of the silicon and aluminum during the first stage because the potassium carbonate being strongly

alkaline dissolves aluminum hydroxide and ortho silicic acid and it is not until this carbonate is very largely converted into bicarbonate, which is almost neutral in reaction, that all of the aluminum and silicon separate out. The reactions are represented, at least in principle, by the following equations:



Of course, carbonation to formation of 100 per cent bicarbonate requires just twice the amount of CO_2 that is needed for the normal carbonate. The speed of carbonation can be greatly increased by distributing the gas uniformly over the whole cross-section of the volume of liquid to obtain the most extensive contact between the gas and liquor, and also by very strong agitation. To the carbonation products we add about one-half ($\frac{1}{2}$) of their volume of water. We then repeatedly filter and wash, the wash water requirements being from two and one-quarter ($2\frac{1}{4}$) to 4 and one-half ($4\frac{1}{2}$) gallons of water per lb. of feldspar digested. These steps, of course, result in the recovery of so much of the potassium from the feldspar as was converted into water soluble compounds during the alkali digestion period.

We convert only a part of the potassium carbonates thus obtained into sales products and the balance we causticize in order to obtain caustic potash for reuse in further digestion operations. In detail, we evaporate the carbonate solution in steps obtaining each time a saturated solution from which, as the temperature is permitted to drop, crystalline masses of potassium carbonate and potassium bicarbonate are obtained, preferably until from five (5) to ten (10) per cent of the total potassium content of the carbonate solution is removed. The potassium carbonates thus obtained also contain the sodium carbonate that is present and thus prevent the building up of the sodium content during repeated reuses of the caustic potash. The balance of the carbonate solution is concentrated to a 10 per cent solution which is suitable for a causticizing operation with lime to produce caustic potash for reuse and calcium carbonate for sale.

To the alumina and silica residue produced by the carbonating we add enough water to make a slurry and then digest the same with from 75 to 125 per cent excess of 95 per cent sulphuric acid, thus placing all

the aluminum salts in solution as alum and aluminum sulphate and rendering the freshly precipitated silica utterly insoluble as SiO_2 , due to the dehydrating action of the sulphuric acid.

The acid digestion products are diluted with water and then the same repeatedly filtered in an acid proof filter and washed, the wash water utilized being about 2.2 gallons per lb. of ore digested.

The aluminum salts in solution are fractionally crystallized, producing as a first fraction practically pure alum containing only traces of iron, the successive fractions containing proportionately more iron and less alum and, of course, more aluminum sulphate. The alum is represented by the formula $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ and the reason for its presence lies in the fact that there is formed in the autoclave a water insoluble but acid decomposable silica containing K_2O and the latter will not appear in the carbonate liquors, but in the residue of alumina and silica, there to be decomposed by the sulphuric acid treatment and thence to follow the aluminum.

The silica is dried of its absorbed and adsorbed water and then cleansed from impurities by treatment with hot concentrated sulphuric acid for one or two hours and then filtered and washed free of acid.

What we claim is:—

1. In a process of separating the constituents of mineral silicates, the steps of recovering the potassium value consisting in, first, converting the silicate into alkali-metal silicate and aluminate by means of a solution of caustic alkali; and then recovering the potassium by passing carbonic acid gas, in the cold and under pressure additional to that normally incident to carbonation, through the silicate and aluminate solution.

2. In the process of separating the constituents of mineral silicates, the steps of recovering the potassium value consisting in, first, converting the silicate into alkali-metal

silicate and aluminate by means of a solution of caustic alkali, and then recovering the potassium by passing carbonic acid gas through the silicate and aluminate solution, the heat generated by carbonation being positively removed and the carbonation being effected under a pressure of substantially 22 inches above atmospheric pressure.

3. In the process of separating the constituents of mineral silicates, the steps of recovering the potassium value consisting in, first, converting the silicate into potassium silicate and aluminate by means of a solution of substantially ninety per cent (90%) caustic potash; and then recovering the potassium by passing carbonic acid gas, in the cold and under pressure additional to that normally incident to carbonation, through the potassium silicate and aluminate solution.

4. In a process of separating the constituents of mineral silicates, the steps which consist in converting the natural ore into an amorphous condition; digesting the same with substantially 90% caustic potash in amount from one and one quarter ($1\frac{1}{4}$) to two (2) times the weight of the ore and an equal weight of water, thus obtaining water soluble potassium silicate and potassium aluminate and water insoluble but acid soluble potassium aluminum silicate; diluting the alkali digestion products with water and carbonating with carbon dioxide to remove the water soluble potassium values; filtering and then digesting the alumina and silica residue with an excess of substantially 95% sulphuric acid to remove the aluminum as soluble salts; and filtering and fractionally crystallizing the aluminum solution, thus obtaining as a first fraction practically pure alum ($K_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$) and successive fractions of alum containing increasing quantities of aluminum sulphate.

5. In a process of separating the constituents of mineral silicates, the steps which consist in converting the natural ore into an amorphous condition; digesting the same with substantially 90% caustic potash in amount substantially two (2) times the weight of the ore and an equal weight of water, thus obtaining water soluble potassium silicate and potassium aluminate and water insoluble but acid soluble potassium aluminum silicate; diluting the alkali digestion products with an amount of water at least equal in volume to said products, and carbonating with carbon dioxide to substantially complete bicarbonation to remove the water soluble potassium values; filtering and then digesting the alumina and silica residue with an excess of substantially 95% sulphuric acid to remove the aluminum as soluble salts; and separating the resultant insoluble silica from the solution of aluminum salts.

6. In a process of separating the constituents of mineral silicates, the steps which consist in crushing the natural ore to substantially thirty-five (35) mesh; converting the crushed ore to an amorphous condition; further crushing the amorphous ore to substantially two hundred (200) mesh; digesting the fine ore with substantially 90% caustic potash in amount from one and one quarter ($1\frac{1}{4}$) to two (2) times the weight of the ore and an equal weight of water, the digestion being effected at a temperature of from 275° to 325° C. and at a pressure of from 300 to 350 pounds per square inch, maintained for substantially two (2) hours, thus producing water soluble potassium silicate and potassium aluminate and water insoluble but acid soluble potassium aluminum silicate; diluting the alkali digestion products with water and carbonating with carbon dioxide to remove the water soluble potassium values; filtering and then digesting the alumina and silica residue with an excess of substantially 95% sulphuric acid to remove the aluminum as soluble salts; and filtering and fractionally crystallizing the aluminum solution, thus obtaining as a first fraction practically pure alum ($K_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$) and successive fractions of alum containing increasing quantities of aluminum sulphate.

7. In a process of separating the constituents of mineral silicates, the steps which consist in converting the natural ore into an amorphous condition; digesting the same with substantially 90% caustic potash in amount substantially two (2) times the weight of the ore and an equal weight of water, thus obtaining water soluble potassium silicate and potassium aluminate and water insoluble but acid soluble potassium aluminum silicate; diluting the alkali digestion products with an amount of water at least equal in volume to said products; and carbonating with carbon dioxide to remove the water soluble potassium values; repeatedly filtering and washing the carbonation products, the wash water requirements being from 2.25 to 4.5 gallons of water per pound of ore utilized; digesting the alumina and silica residue with from 75% to 125% excess of substantially 95% sulphuric acid to remove the aluminum as soluble salts; and filtering and fractionally crystallizing the aluminum solution, thus obtaining as a first fraction practically pure alum ($K_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$) and successive fractions of alum containing increasing quantities of aluminum sulphate.

Signed by me this 4th day of May, 1922.

SHERMAN W. SCOFIELD.

Signed by me this 13th day of May, 1922.

JOHN B. LA RUE.