UNITED STATES PATENT OFFICE.

FRANK K. CAMERON, OF SALT LAKE CITY, UTAH, ASSIGNOR TO ALASKA PRODUCTS COMPANY, OF NEW YORK, N. Y., A CORPORATION OF SOUTH DAKOTA.

PROCESS OF RECOVERING POTASSIUM SALTS.

1,259,486. Specification of Letters Patent. Patented Mar. 19, 1918.

No Drawing. Application filed May 9, 1917. Serial No. 167,472.

To all whom it may concern:

Be it known that I, FRANK K. CAMERON, a citizen of the United States, residing at Salt Lake City, in the county of Salt Lake and State of Utah, have invented certain new and useful Improvements in Processes of Recovering Potassium Salts, of which the following is a specification.

This invention relates to processes of recovering potassium salts; and it comprises a method of treating kelp wherein kelp which is advantageously freshly cut, is comminuted and submitted to what may be termed a homogenizing or pulping treatment, the raw pulp is treated with a little acid or the like to neutralize it and cause a separation of liquor from the insoluble solids and this liquor is directly evaporated to obtain potassium chlorid; all as more fully hereinafter set forth and as claimed.

The manufacture of potassium salts from seaweed, or kelp, is of course a very old industry, but it was substantially abandoned until recent emergencies raised the price of potash to a high point. This was because of the cost of operation. Practically all the propositions involve drying the wet seaweed, either by artificial heat or by sun heat, and then charring or burning the dried material. Seaweed is a wet, very bulky material and when it is dried by exposure to the air much handling as well as space is required while if it be dried artificially in roasters and the like the consumption of fuel is inordinate. In burning the dried material it is either merely charred or completely burnt. In either case leaching is necessary and this leaching is also expensive. If the weed be charred the salts are retained but extraction from the char is difficult while if burning be complete to get rid of carbon, much of the available salts is volatilized. For these reasons among others, the extraction of potassium compounds from seaweeds has not proved profitable under modern conditions except where the price of potassium compounds becomes very high. Occasionally it has been proposed to express the seaweed to obtain a liquid which could be evaporated and the residue burnt. From the physical character of the seaweed this has not proved successful in practice.

In the present invention I have provided a simple, cheap and ready method of extracting the potassium values from the seaweeds without manual handling and with the recovering of valuable byproducts. I have found that the potassium content of the seaweed is for the most part in solution and while there are many organic compounds of more or less gummy or slimy nature also in solution that these may be readily separated, giving a liquid which is pure enough to allow direct evaporation in modern types of evaporators such as multiple effects. In the present invention, I use the seaweed as fresh as may be since I find if it be allowed to remain out of water for any length of time it is more difficult for me to treat. It may, however, be kept in seawater until needed, or until decay of the cell tissue commences. This seaweed I comminute and pulp as finely as possible, giving me a more or less pasty mixture. I have found that if this mixture in a raw state be treated with a little acid or other astringent, just about enough to neutralize it so as to give a neutral indication to neutral tint litmus, the "algin" substances separate carrying with them practically all the organic matter and many of the mineral matters which are not here desired. I find it preferable to use hydrochloric acid although sulfuric acid or other coagulating agents may be employed.

The seaweed as it is cut consists of leaves and stems and may be of several different varieties. Some portions of the mass lend themselves to filtration operations more readily than others and I find it advantageous therefore to treat the seaweed in a methodical manner in performing the above stated operation. It is best to take the fresh seaweed and chop or cut it as fine as practicable, consistent with easy operation, and then run the minced mass through some type of pressing device with perforated plates or the like, adapted to retain merely the coarser matter; the fibrous parts and components of

the seaweed. Removal of these portions at this stage reduces the amount of coagulum to be subsequently separated; and these portions may also with advantage be used in treating the coagulum itself in a manner hereinafter described. I have found advantageous the type of continuous presses having coned perforated elements. On running the minced mass of seaweed through such a press it is separated into a portion of a more fibrous character which is separated and delivered by the press; and a pulpy mass or magma which flows or exudes through the perforations. This pulpy mass or magma I place in suitable vats or tanks, and to it I add a little hydrochloric acid. As stated, other coagulating agents may be used but I find that as a rule with most seaweed materials hydrochloric acid gives me the best results. In using hydrochloric acid not much is necessary; I do not ordinarily add enough to produce any distinct acidity. The best results are obtained in using enough hydrochloric acid with the magma to produce a separated liquor which will appear neutral in reaction to "neutral tint" litmus paper. The material itself will indicate the right amount of acid since the color, with the right amount, becomes a faded grayish yellow. After the acidification, the magma separates into two portions, an underlying layer of liquid and a floating blanket of coagulum. I may allow the mass to stand for several hours to promote this separation, or what is much the same, I may deliver acid treated magma continuously into the top of a tank while slowly and continuously withdrawing clarified liquor at the bottom. Floating of the coagulum is largely due to entangled air and gases; it will again fall if the magma be allowed to stand too long. For this reason the coagulating treatment is best effected at once after mincing.

There are many other acid reacting coagulating or flocculating agents which I may use in lieu of hydrochloric or sulfuric acid, such as aluminum sulfate, iron chlorid, etc., for neutralizing the basic bodies present, but they have ordinarily no advantage over hydrochloric acid and furthermore are not as desirable, particularly where sulfuric acid salts are employed, for the reason that I propose regaining my potassium as potassium chlorid as free as may be from sulfates and other salts.

The settled liquor may be sent directly to multiple effects and evaporated to the crystallizing point, giving a crop of salts rich in potassium chlorid and containing only a minor amount of sodium chlorid. These crystallized salts may be afterward treated in ordinary ways to obtain pure potassium chlorid. The liquor is so free of organic matter and scale giving constituents that after crystallization is effected the separated salts may be drained in a centrifugal and the mother liquor returned for reëvaporation.

The blanket formed in the flocculating or coagulating stage because of its physical properties is rather difficult to press; and it is better to rely on natural separation to effect the recovery of the liquor contained in it. It may however be drained on perforated plates, wire gauze, etc. A better method of disposition is to return it to the minced mass going through the coned presses. Here its solid matters are in large part separated by and with the coarser more or less fibrous matters of the original minced mass and such as go through with the pulp are again collected in the floating blanket for return.

In its best embodiment therefore my method comprises mincing fresh seaweed, passing the raw minced material through pressing devices adapted to retain coarser or fiber-like portions, coagulating the raw pulp or magma, separating the blanket of coagulum from the clear liquor and returning the coagulum to fresh minced material for repassage through the presses, and directly evaporating the separated liquor to produce crystallized potassium chlorid.

The solid matter separated in the coagulating operation may be treated to regain valuable byproducts. The composition of the blanket depends somewhat upon the particular way in which the mincing operation is conducted. If the blanket be returned to the coned, perforated homogenizer in the way hereinbefore mentioned, the solid matters discharged by the homogenizer will of course be a mixture of the fiber-like material and of coagulum. If it be so returned the coagulum solids will not contain so much of the fibrous matter. The solids of the separated blanket may be regarded as consisting of cellular tissue or woody matter, separated alginates and other less definite substances. By treating it with a little caustic soda (other alkalis seem to be less satisfactory) the alginic acid goes into solution. By separating the liquor from the solid matter a clear solution of sodium alginate may be produced. This may be evaporated down to give a salt-like complex or alginate. Or it may be acidulated with sulfuric acid throwing "alginic" acid out of solution and forming a solution of sulfate of soda. The residual solids after the extraction of the alginic acid may be used for cellulose purposes. They may, for instance, be dried and used as a light heat-retaining casing for piping.

With a typical giant kelp from the American shores of the Pacific Ocean a yield of

about 190 gallons of clear juice may be obtained from a ton. On chopping and mincing the fresh seaweed in the manner hereinbefore described a sort of magma is obtained. On treating this raw magma with hydrochloric acid to a point short of obvious acidity to neutral tint litmus, which requires about 0.25 per cent. of commercial concentrated acid, a rapid coagulation takes place, giving a blanket of separated solids and a layer of clear juice or liquor. Whether the blanket goes to the top or settles, depends largely upon the mechanical means employed in mincing and the like. Floating is caused by included air and gases, and it is better to work in such a manner that there is considerable aeration during the pulping in order to produce a floating blanket. As stated, it is difficult to separate the liquor and the coagulum by ordinary mechanical means, such as pressing, and the fact that if the pulp or magma is well aerated the mixture will separate of itself, is of great technical importance. Therefore, the effort should be to employ mechanical means in the mincing step which will give as much aeration as possible. The extent to which the blanket contracts, *i. e.*, the relation between the volume of the blanket and the volume of clear liquor, depends upon the length of time the mixture is allowed to stand after the addition of the acid or other coagulant; the extent of aeration and many other factors. The more intimate and uniform the aeration has been the quicker will be the separation. The ideal condition is to have minute air-bells thoroughly distributed through the solid matters. Usually, after acidulating and allowing the mass to stand for about 30 minutes, the floating blanket of coagulum will appear to occupy about 30 per cent. of the total volume. By standing longer blanket contracts further and the volume of clear liquid obtained is considerably increased. This liquid runs about 1.035 specific gravity. It may be less and it may be greater but generally is of about this density. With such a density the liquor will contain around 6 per cent. of total solids of which perhaps 1 per cent. will be residual organic matter. About half the solid matter usually is potassium chlorid. The ratio of KCl to NaCl is about 2:1; that is with such a liquor containing about 6 per cent. total solids and 3 per cent. KCl, there will be about 1.5 per cent. NaCl. The amount of organic matter in solution is generally, after the treatment described not to exceed 1 per cent., an amount which is not great enough to interfere materially with evaporation and crystallization. The liquor upon evaporation may be made to yield successive crops of crystals. The particular composition of each crop of course depends upon the circumstances of evaporation and the temperature at which crystallization takes place, it being borne in mind that KCl is more soluble in hot liquor than in cold while NaCl is of even less solubility in hot liquids than in cold liquids, when the solution also contains much KCl.

Potassium chlorid may be readily separated by recrystallization in a commercially pure state, and very readily, by treating known amounts of the mixed salts with definite amounts of water at alternating hot and cold temperatures.

Any ordinary type of evaporator working under vacuum or under plus pressure, or both, may be employed. It is advantageous to use the ordinary types adapted for the manufacture of salt. The various crops of crystals obtained may be readily drained in a centrifugal.

What I claim is:—

1. The process of recovering potassium salts from kelp which comprises mincing the kelp to form a magma, treating the magma thus produced with an acid agent in merely the quantity sufficient to flocculate suspended solids and produce a coagulum, separating the coagulum and the liquor, and evaporating the liquor to crystallization.

2. The process of recovering potassium salts from kelp which comprises mincing the kelp to form a magma, treating the magma thus produced with hydrochloric acid in merely the quantity sufficient to flocculate suspended solids and produce a coagulum, separating the coagulum and the liquor, and evaporating the liquor to crystallization.

3. The process of recovering potassium salts from kelp which comprises mincing the kelp to form a magma, separating the coarser and fibrous-like portions of the magma, adding an acid flocculating agent to produce coagulum and a separation of liquor, returning the coagulum to fresh minced material and evaporating the liquor to crystallization.

4. The process of recovering potassium salts from kelp which comprises mincing the fresh kelp, pressing the minced material through coarse perforations to produce a homogenized magma with some separation of coarse and fibrous material, adding an acid flocculating agent to the homogenized magma to produce a coagulum and separation of liquor, returning the coagulum to fresh minced material for separation and homogenization and evaporating the liquor to crystallization.

5. The process of recovering potassium salts from kelp which comprises mincing and straining the kelp in such a manner as to produce thorough aeration, adding an

acid flocculating agent to produce a floating separation of coagulum from the clear liquor, returning the floating coagulum for treatment together with fresh kelp in the straining operation and evaporating the liquor to crystallization.

6. The process of recovering potassium salts from kelp which comprises comminuting the kelp to form a thoroughly aerated substantially uniform magma, treating this magma with an acid flocculating agent to form a floating separation of air-buoyed solids, and evaporating the separated liquor to crystallization.

In testimony whereof, I affix my signature hereto.

FRANK K. CAMERON.