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PROCESS FOR RECOVERING POTASSIUM SALTS FROM MINERALS

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This invention described herein may be manufactured and used by or for the Government for governmental purposes, without the payment to us of any royalty thereon.

This invention relates to a method of treating complex potassium minerals or salts for the purpose of manufacturing a product of relatively high potassium content.

The primary object of the invention is the recovery of potassium salts in a valuable concentrated form from the mineral polyhalite

$(K_2SO_4.MgSO_4.2CaSO_4.2H_2O)$

which is known to exist in extensive deposits in a region in the southwestern United States. The method of recovery disclosed may, however, also be applied to similar potassium minerals or salts, such as krugite, langbeinite, schönite, leonite, syngenite, or to any mixture comprising potassium sulphate with magnesium sulphate and/or calcium sulphate.

The reduction of simple sulphates, such for example as barium sulphate, by means of suitable reducing agents is old art, but no evidence concerning the behavior of double or triple salts containing potassium sulphate upon reduction is known with the exception of one laboratory reference by Schumann (Ann. 187, 286–321 (1877) p. 306). Schumann noted that the double sulphate of potassium and magnesium was reduced by hydrogen at a red heat and assumed from his qualitative experiments that K_2S and MgO were the products obtained. No quantitative data were recorded by this investigator.

It is not possible to state definitely from this experiment or from any other disclosure in the prior art that a satisfactory recovery of potassium compounds would be obtained by a reduction method even in the case of the double sulphate of potassium and magnesium. In the case of polyhalite, which is a triple sulphate of potassium, magnesium, and calcium, prediction of results could be no more than a hypothesis.

We have discovered that by maintaining a reducing agent in contact with polyhalite at a moderately high degree of heat for a desirable period of time the polyhalite is so modified that on subsequent extraction with water practically all of the potassium compounds contained in the reduction product goes readily into solution, while practically no calcium or magnesium compounds are dissolved; that an extract solution highly concentrated with respect to potash may thereby be obtained; and that evaporation of this extract solution yields desirable potash compounds.

For example, when polyhalite, ground to pass a screen with 10 meshes to the linear inch, is heated in contact with a stream of hydrogen, the polyhalite is decomposed, with hydrogen sulphide, water vapor and free sulphur present in the waste gas. While reduction may take place slowly at lower temperatures, it first becomes evident at a temperature of approximately 650° C. The rate of reduction increases with increase in temperature. This increase is particularly noticeable in the range from 800 to 900° C. The volatilization of potassium compounds is small in this temperature range, but increases rapidly with increase in temperature above approximately 1000° C. It is therefore desirable to maintain a temperature between 800° and 1000° C. during reduction. A temperature of 900° C. has been found suitable since it results in a rapid rate of reduction with little loss of potassium compounds by volatilization. It is obvious, however, that the reduction might be carried out in practice at a somewhat higher or somewhat lower temperature.

Experiments have shown that when polyhalite is heated at approximately 900° C. in a stream of dry carbon monoxide, practically no reduction takes place although the polyhalite is in the fluid state. If, however, a mixture of carbon monoxide and water vapor is used under otherwise similar conditions the polyhalite is readily reduced. Satisfactory reduction is likewise accomplished by the similar use of a mixture of carbon monoxide and hydrogen or a mixture of carbon monoxide, hydrogen and water vapor.

We have also discovered that when natural gas in which methane is the chief constituent is passed over polyhalite heated at approximately 900° C. in the substantial absence of water vapor, polyhalite is reduced, but carbon is deposited in considerable quantities. If, however, a mixture of this natural gas and water vapor is used under otherwise similar conditions the polyhalite is reduced without appreciable carbon deposition.

Experiment has further shown that when an intimate mixture of polyhalite and carbon is heated at approximately 900° C. the polyhalite is reduced, and that this process of reduction may be facilitated by blowing water vapor through the heated mixture.

We have found that the potassium compounds present in the reduced material are easily and completely extracted by water. Water at ordinary atmospheric temperature may be used, but hot water has been found to be preferable. The potassium concentration of the extract liquor is limited by mechanical problems in the sep-

aration of the extracted solid, rather than by the solubility of the potassium compounds present, which is very high. For example, we extracted 40 grams of reduced polyhalite with 50 grams of water at 100° C. for 30 minutes. The solid residue was separated by filtration, and the filtrate was then used to extract an additional 36 grams of reduced polyhalite. The filtrate from this second stage contained 28 per cent K, 16.9 per cent total sulphur, and no Ca, Mg, or SO_4. The solid residue from the first stage, after washing with 50 grams of water and drying at 110° C., contained only 0.22 per cent K, showing that the recovery of potassium compounds during extraction was very complete.

On evaporating the extract liquors rich in potassium small amounts of such compounds as K_2SO_4 and K_2SO_3 are first deposited. When evaporated to dryness the major portion of the potassium is obtained in the form of an essentially sulphide material, which upon being dried at 110° C. may contain 50 per cent K, and when fused to drive off water may contain 64 per cent K. For example, when 630 grams of reduced polyhalite were extracted with 630 grams of water at the boiling point for 10 minutes, and the solid residue was separated by filtration, a concentrated extract was obtained. After 80 per cent of the extract had been evaporated, only 6 grams of solid material, consisting of K_2SO_4 and K_2SO_3 had been deposited from solution. On evaporating the remaining solution to dryness and drying at 110° C., 124 grams of material were obtained which contained 51.0 per cent K, 26.3 per cent total sulphur, 20.4 per cent H_2O, and no compounds of calcium or magnesium.

Similar results were obtained by washing the solid residue from the above extraction with 630 grams of cold water, and filtering off the final solid residue. After 80 per cent of the wash filtrate had been evaporated, only 3 grams of solid material, consisting of K_2SO_4 and K_2SO_3, had been deposited from solution. On further evaporation until 95 per cent of the filtrate has been evaporated, an additional 2 grams of solid material had deposited. On evaporation of the remaining solution to dryness and drying at 110° C. 91 grams of material were obtained which contained 50.9 per cent K, 26.4 per cent total sulphur, 19.8 per cent H_2O, and no compounds of calcium or magnesium.

Since polyhalite, a triple sulphate of potassium, magnesium and calcium, has been found to yield its potassium content readily upon extraction following reduction, it may reasonably be assumed that krugite

$$(K_2SO_4.MgSO_4.4CaSO_4.2H_2O),$$

which differs from polyhalite only in possessing a greater content of $CaSO_4$, will yield similar desirable results. It may also be assumed that the less complex minerals or salts, langbeinite

$$(K_2SO_4.2MgSO_4),$$

schönite ($K_2SO_4.MgSO_4.6H_2O$) and leonite

$$(K_2SO_4.MgSO_4.4H_2O),$$

which contain only potassium sulphate and magnesium sulphate with no calcium sulphate will yield their potassium content when treated in essentially the manner disclosed. Likewise, syngenite ($K_2SO_4.CaSO_4.H_2O$), which contains only potassium sulphate and calcium sulphate with no magnesium sulphate might reasonably be assumed to respond in a manner similar to polyhalite. Mixtures of such minerals or salts, or of the constituent simple sulphates would not differ essentially in behavior. Satisfactory separation of potassium compounds by reduction and extraction of any such minerals or salts or mixtures would be reasonably expected by any person skilled in the art.

The method of treatment, examples of which are given above, comprises relatively simple operations which may be performed efficiently and economically on an industrial scale by one skilled in the art. Since each one of the necessary operations may be performed by various means, and since control of these operations within narrow limits is not essential in obtaining desirable results, the scope of the invention should not be construed as being limited by the specific examples used above in an illustrative manner.

We have shown that by reducing polyhalite and subsequently extracting the reduction product with water it is possible to separate the potassium compounds from calcium and magnesium compounds in a simple and efficient manner, yielding a product highly concentrated with respect to potassium.

Having described our invention, what we claim as new and wish to secure by Letters Patent is:

1. The process of manufacturing potassium salts which comprises reducing a material containing potassium sulphate, magnesium sulphate and calcium sulphate by means of a suitable reducing agent at a moderately high degree of heat to yield a reduction product containing potassium sulphide together with calcium compounds and magnesium compounds substantially insoluble in water; extracting this reduction product with water to yield a liquor containing essentially potassium sulphide with practically no compounds of calcium or of magnesium; and recovering solid potassium salts from this liquor by known means.

2. The process of manufacturing potassium salts which comprises reducing a material containing potassium sulphate and magnesium sulphate by means of a suitable reducing agent at a moderately high degree of heat to yield a reduction product containing potassium sulphide together with magnesium compounds substantially insoluble in water; extracting this reduction product with water to yield a liquor containing essentially potassium sulphide with practically no compounds of magnesium; and recovering solid potassium salts from this liquor by known means.

3. The process of manufacturing potassium salts which comprises reducing a material containing potassium sulphate and calcium sulphate by means of a suitable reducing agent at a moderately high degree of heat to yield a reduction product containing potassium sulphide together with calcium compounds substantially insoluble in water; extracting this reduction product with water to yield a liquor containing essentially potassium sulphide with practically no compounds of calcium; and recovering solid potassium salts from this liquor by known means.

4. The process of manufacturing potassium salts which comprises reducing polyhalite by means of a suitable reducing agent at a moderately high degree of heat to yield a reduction product containing potassium sulphide together with calcium compounds and magnesium compounds substantially insoluble in water; extracting this reduction product with water to yield a liquor containing essentially potassium sulphide

with practically no compounds of calcium or of magnesium; and recovering solid potassium salts from this liquor by known means.

5. The process of manufacturing potassium salts which comprises reducing polyhalite by means of a suitable reducing agent at a moderately high degree of heat to yield a reduction product containing potassium sulphide together with calcium compounds and magnesium compounds substantially insoluble in water; extracting this reduction product with hot water to yield a liquor containing essentially potassium sulphide with practically no compounds of calcium or of magnesium; and recovering solid potassium salts from this liquor by known means.

6. The process of manufacturing potassium salts from polyhalite which comprises reducing polyhalite at a temperature in the range from 800 to 900° C. by means of hydrogen to yield a reduction product containing potassium sulphide together with calcium compounds and magnesium compounds substantially insoluble in water; extracting this reduction product with hot water to yield a liquor containing essentially potassium sulphide with practically no compounds of calcium or of magnesium; and recovering solid potassium salts from this liquor by known means.

7. The process of manufacturing potassium salts from polyhalite which comprises reducing polyhalite at a temperature in the range from 800 to 900° C. by means of a gaseous reducing agent containing carbon monoxide and hydrogen to yield a reduction product containing potassium sulphide together with calcium compounds and magnesium compounds substantially insoluble in water; extracting this reduction product with hot water to yield a liquor containing essentially potassium sulphide with practically no compounds of calcuim or of magnesium; and recovering solid potassium salts from this liquor by known means.

8. The process of manufacturing potassium salts from polyhalite which comprises reducing polyhalite at a temperature in the range from 800 to 900° C. by means of a gaseous reducing agent containing carbon monoxide and water to yield a reduction product containing potassium sulphide together with calcium compounds and magnesium compounds substantially insoluble in water; extracting this reduction product with hot water to yield a liquor containing essentially potassium sulphide with practically no compounds of calcium or of magnesium; and recovering solid potassium salts from this liquor by known means.

9. The process of manufacturing potassium salts from polyhalite which comprises reducing polyhalite at a temperature in the range from 800 to 900° C. by means of a gaseous reducing agent containing carbon monoxide, hydrogen, and water vapor to yield a reduction product containing potassium sulphide together with calcium compounds and magnesium compounds substantially insoluble in water; extracting this reduction product with hot water to yield a liquor containing essentially potassium sulphide with practically no compounds of calcium or of magnesium; and recovering solid potassium salts from this liquor by known means.

10. The process of manufacturing potassium salts from polyhalite which comprises reducing polyhalite at a temperature in the range from 800 to 900° C. by means of a gaseous reducing agent initially containing natural gas and water vapor to yield a reduction product containing potassium sulphide together with calcium compounds and magnesium compounds substantially insoluble in water; extracting this reduction product with hot water to yield a liquor containing essentially potassium sulphide with practically no compounds of calcium or of magnesium; and recovering solid potassium salts from this liquor by known means.

11. The process of manufacturing potassium salts from polyhalite which comprises reducing polyhalite at a temperature in the range from 800 to 900° C. by means of carbon and water vapor to yield a reduction product containing potassium sulphide together with calcium compounds and magnesium compounds substantially insoluble in water; extracting this reduction product with hot water to yield a liquor containing essentially potassium sulphide with practically no compounds of calcium or of magnesium; and recovering solid potassium salts from this liquor by known means.

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