CONCENTRATION OF RADIUM FROM CARNOTITE ORES

B. S. Hopkins and G. C. Ruhle, University of Illinois

Carnotite is a potassium uranyl vanadate of essentially the composition represented by the formula $K_2O.2UO_3.V_2O_5.8H_2O$. All the mineral substances present are valuable, but the most valuable component, radium, is present in such a small proportion that it cannot be shown readily in the formula. It requires a ton of relatively rich carnotite ore to produce 10 milligrams of radium. It is very evident then that any method which is efficient in the removal of radium must be capable of effecting practically 100 per cent extraction. It is also clear that a very important part in the process will consist in the concentration of the minute quantities of radium after they have been removed from the great bulk of the ore.

For the first step in the process, the United States Bureau of Mines recommends the employment of nitric acid, by the use of which practically all the radium together with most of the other valuable mineral constituents present is converted to the soluble form. The solution obtained in this manner is nearly neutralized, barium chloride is added, and the radium and barium are precipitated by adding sulfuric acid. The precipitated radium—barium sulfate is filtered off, and from the clean solution uranium is precipitated, usually as sodium uranate and the vanadium either as ferrous vandate or calcium vanadate.

The main advantage claimed for this process is the high recovery of radium. The disadvantages arise from the cost of nitric acid and the fact that there is only partial extraction of vanadium. In large measure the cost difficulty is overcome by the fact that a very considerable portion of the nitric acid may be recovered and used again. If the main object in view is the extraction of radium, this method is said to be especially efficient.

The radium-barium sulfate, which contains only a very small per cent of radium, must now be subjected to treatment for the concentration of radium. The usual pro-

cedure is as follows: The mixed sulfates are reduced to sulfides by heating with charcoal or are converted to the carbonates by boiling with sodium carbonate solution. The sulfides or carbonates so obtained are dissolved in hydrochloric acid and the resulting solutions subjected to fractional crystallization. This method of concentration depends upon the fact that when a saturated solution of radium-barium chloride is cooled from 100° to 0° the crystals formed are much richer in radium than the original solution. Accordingly, if a solution of the mixed chlorides is evaporated until there remains not quite enough solvent to keep all the salts in solution, there will be a tendency for the radium chloride to crystallize out, while the mother liquor will become correspondingly richer in barium chloride. After this process has been repeated many times, it is found that the radium is nearly all concentrated in the crystal fractions, while the solutions at the "soluble end" of the series contain no radium. It has been found that the concentration of radium takes place more rapidly if this process of fractional crystallization is carried out by the use of bromides in place of chlorides. This is explained by the fact that the bromides are more soluble than the chlorides. If a saturated solution of the chlorides is cooled from 100° to 0°, about 50 per cent of the solute crystallizes out; but under the same conditions the bromide solution will give up only about 34 per cent of the salts. Hence, there is a more rapid concentration of the radium if this salt is used.

The concentration of the radium in any fraction may be calculated from the equation:

$$C = AK^n$$

in which n is the number of crystallizations, A is either the actual or assumed concentration of some dish to start with, and K, called the enrichment factor, is a constant when the crystallizations are carried out under exactly similar conditions. It represents the relative concentration of the radium in the crystals to that in the original material. It has been shown[1] that the enrichment factor is practically independent of the degree of

---

1. John L. Niermann. Jour. Phys. Chem. 24, 192 (1920).

acidity of the mother liquor; likewise[2] that this factor
for a bromide system is 2.6 while for a chloride system
it is about 1.6. Reasoning from the familiar relation-
ships shown in the periodic table, it might readily be
concluded that if a bromide system was more efficient
than a chloride system the fractional crystallization of
the iodides would be considerably more efficient than
either the chloride or the bromide. With this view point
in mind a series of experiments are now being conducted
to determine the practicability of an iodide system of
radium concentration.

Before this experiment could be carried out success-
fully, it was necessary to determine the best method of
preparing the iodide solution. Several methods were
tried such as: (1) Superheated steam was passed over
the sulfide, converting it to the hydroxide, which was
then heated to a dull red in a stream of hydriodic acid
gas; (2) the sulfide was transformed to the iodide by
boiling with an alcoholic solution of iodine; (3) the sul-
fide was added to a boiling solution which contained
slghtly more than the calculated amount of ferrous io-
dide; (5) the sulfide was boiled with hydriodic acid solu-
tion and a small amount of iodine in hydriodic acid was
added. Of these methods, the last proved to be the most
satisfactory, so it was employed.

To test out the efficiency of the halide fractionation
system, three samples of radium-barium sulfate, each
weighing 100 grams, were reduced with charcoal and the
resulting sulfides were treated with hydrochloric, hydro-
bromic and hydriodic acids respectively. After the ac-
tion had ceased they were boiled to expel hydrogen sul-
fide, filtered and the residue washed thoroly. The fil-
trates were evaporated to dryness, taken up with a small
quantity of water to which was added a little of the free
acid, and the fractional crystallization begun, by evapor-
ating on a steam bath until the solutions were completely
saturated. Then the dishes were cooled in ice water, the
crystals filtered out, redissolved in pure water and re-
crystallized.

2. C. E. Scholl. Jour. Am. Chem. Soc. 42, 889 (1920).

To test the efficiency of the solvent action of the three halogen acids, the residues from the acid extractions were analyzed for their barium content and were found to contain practically the same per cent of that element. Hence, it was concluded that the acid extraction was the same in all cases and that the three solutions presumably contained the same amount of radium.

After several crystallizations of the three halide systems, equivalent amounts of the richest fraction of each were placed in the case of a charged electroscope and the time of discharge noted. The iodide discharged the electroscope more quickly than either the chloride or the bromide, but the work has not yet progressed to the point which will permit a definite statement concerning the value of its enrichment factor. Another decided advantage in the use of the iodide comes from the greater solubility of this salt over the others; hence a given amount of radium in the iodide solution occupies a much smaller volume than it does in the chloride or bromide solution. This permits the use of smaller crystallizing dishes, a material saving on a large scale operation.

The use of the iodide for radium concentration would not be practical unless it were possible to recover a large per cent of the iodine at the end of the process. Accordingly, when the radium had been practically all removed from certain fractions, the barium iodide solutions were saturated with chlorine. The displaced iodine was filtered off, dried and resublimed. The barium chloride solution was evaporated and the crystals were used in the precipitation of the next batch of radium-barium sulfate. The iodine was mixed with a little less than the theoretical amount of red phosphorus, and water was slowly dropped over the mixture. In this manner hydriodic acid was obtained, which was also used in the next series. The recovery was satisfactory, indicating that the operating cost for iodine would be quite reasonable.

Urbana, Illinois, April 25, 1922.