

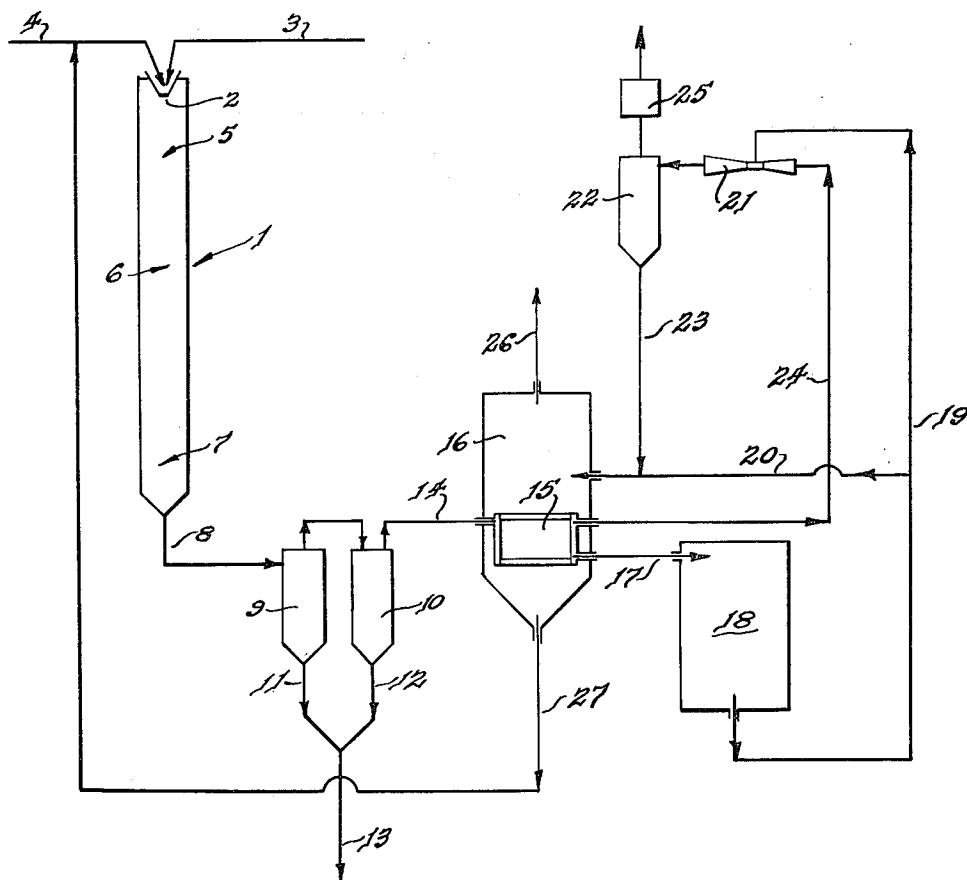
Nov. 14, 1961

B. M. JOHNSON, JR., ET AL

3,008,904

PROCESSING OF RADIOACTIVE WASTE

Filed Dec. 29, 1959



INVENTORS
Benjamin M. Johnson, Jr.
Gerald B. Barton

BY

Roland A. Anderson

Attorney

1

3,008,904

PROCESSING OF RADIOACTIVE WASTE

Benjamin M. Johnson, Jr., and Gerald B. Barton, Kennewick, Wash., assignors to the United States of America as represented by the United States Atomic Energy Commission

Filed Dec. 29, 1959, Ser. No. 862,732

2 Claims. (Cl. 252—301.1)

This invention deals with the processing of radioactive waste solutions as a preparation for disposal.

Radioactive waste solutions are obtained in all kinds of separation processes in which uranium or plutonium or other actinide elements are recovered from neutron-irradiated uranium. These recovery methods can be based on solvent extraction, on precipitation or on adsorption. The aqueous waste solutions left after such separation processes contain the bulk of the radioactive fission products in a highly dilute form, also salts, such as aluminum nitrate and sodium nitrate, that have been added or formed, for instance, for salting-out purposes; they possibly also contain reducing and/or oxidizing agents that were added for the conversion of actinides from one to another valence; and as a consequence they may also contain decomposition products formed by reaction of the reducing or oxidizing agents, and in addition they will probably contain corrosion products.

These dilute waste solutions as such are not suitable for disposal; they are too voluminous and hazardous. Furthermore the presence of the radioactive ingredients in liquid form could gradually contaminate the surroundings by diffusion in the event of container failure. It is necessary to reduce the bulk of the waste solutions and to convert the radioactive fission products into a water insoluble form, for instance, by dehydration and calcination, respectively.

The processes used heretofore for the dehydration and calcination of radioactive waste solutions showed a number of disadvantages. A great amount of the solid material formed by the dehydration was entrained by the off-gas in the form of dust, and this, in turn, required more elaborate equipment to protect the personnel from the radioactivity than would be required if all radioactive products remained in the apparatus proper in liquid or solid form.

It is an object of this invention to provide a process for the dehydration and calcination of radioactive waste solutions by which the above-mentioned disadvantages are overcome.

It is thus an object of this invention to provide a process for the dehydration and calcination of radioactive waste solutions in which dust formation and entrainment of radioactive materials by the off-gas are reduced to a minimum.

It is another object of this invention to provide a process for the dehydration and calcination of radioactive waste solutions in which comparatively little treatment of the off-gas is required.

It is another object of this invention to provide a process for the dehydration and calcination of radioactive waste solutions by which the product obtained is a free-flowing powder of high density and low water solubility.

It is finally also an object of this invention to provide a process for the dehydration and calcination of radioactive waste solutions which is economical as far as power consumption for heating is concerned.

It was found that, by spraying the waste solution into a calciner that is brought to elevated temperature with heat radiated by the calciner walls, calcination results were better than when the solution was heated by other means; the product then was free of lumps and fluid occlusions. The use of a spray calciner has the advantage

2

that there is little hold up in the system. The calciner never has a large bulk of material therein which would remain in it should operation be stopped. It was also found that, by adding phosphate, silicate and/or borate to the waste solution prior to the radiant-heat spray calcination, a product of increased density was obtained which, after melting, had a glasslike consistency and was considerably less soluble in water than was the calcined product without melting. Improved thermal conductivity resulted from the increased density. The product obtained is a powder consisting of beads which had melted and solidified in the calciner. These beads have an average size of about 10 microns.

Finally, it was discovered that, by dissolving in the waste solution sugar or any other combustible water-soluble organic material and decomposing said combustible material during the process to form carbon, ignition of the latter furnishes enough heat to bring the particles to a high temperature in the chamber of the calciner without the necessity of heating the calciner walls to unfavorably high temperatures. The combustion heat furnished by the oxidation of the sugar carbon thus brings about calcination and melting of the dehydrated particles and yields a product of reduced surface area and increased density. The very best results were obtained by adding both sugar or other combustible organic substance and phosphate, silicate and/or borate to the waste solution, because the two types of materials have a favorable synergistic effect on the properties of the final product.

The process of this invention thus comprises adding a water-soluble phosphate, silicate and/or borate to a radioactive aqueous waste solution, spraying the solution thus obtained in a heated space whereby water is evaporated and a dry product is formed and the dry product subsequently is calcined and melted, and separating the melted product from the water vapor and volatile gaseous products formed.

While the process can be applied to acidic, neutral and alkaline solutions, a nonacidic solution was found preferable, because then less ruthenium, one of the fission products usually present, is volatilized with the off-gas and also because a final product of lower water solubility is then obtained.

In the preferred embodiment of the process of this invention, the waste solution is introduced into a tower having zones of successively increasing temperature for successive dehydration and calcination. Atomizing is best carried out in the absence of air; however, satisfactory results were also obtained when air was present. The tower is heated to ignition temperature prior to atomization in order to bring about the desired reactions of dehydration and calcination. As the spraying gas, steam was the preferred medium, because it can be condensed easily and the off-gas volume thus can be considerably reduced; this is not possible if spraying is carried out, for instance, with air.

The temperatures for the various zones are not highly critical; however, in order to obtain optimal results, the temperature should be from about 325 to 400° C. near the spraying nozzle and from about 800 to 1000° C. in about the center of the tower, the calcination zone. At this latter temperature range, calcination is carried to completion and the calcined particles are melted whereby the density of the product is increased. The particles do not agglomerate because the suspension is quite dilute. The bottom of the tower was preferably maintained at about 300° C. Addition of phosphate, borate or silicate ions is generally necessary to obtain melting at these temperatures.

The residence time of the material in the reaction chamber, for quantitative reaction, should be from 10 to 20 seconds. It was found that during reaction a tempera-

ture gradient did not exist within the cross section of any zone of the tower, which proves that rapid heat interchange takes place between the radical zones of different temperatures within one zone.

In the accompanying drawing one apparatus that was preferred by the inventors for carrying out the process is illustrated diagrammatically.

Referring to this drawing in detail, the reference numeral 1 designates a dehydration and calcination tower, a "calciner" which is equipped at its top with a fluid-spray nozzle 2. An inlet pipe 3 for steam and an inlet pipe 4 for the waste solution to be treated lead into said spray nozzle 2. The tower has a dehydration zone 5, a calcination zone 6 and a cooling zone 7. To create these zones, independent heating means (not shown) arranged around zones 5 and 6 and cooling means (also not shown) arranged around zone 7 are operated. At the bottom of the tower there is an outlet pipe 8 which leads to a cyclone 9, and the cyclone, in turn, is connected in series with a glass-bag filter 10. Discharge pipes 11 and 12 of the cyclone and the glass filter respectively, lead to a common pipe 13 through which the solids deposited at the bottoms of the cyclone 9 and the glass-bag filter 10 are withdrawn and charged to a packaging unit (not shown).

At the top of filter 10 there is arranged a pipe 14 which is connected with a heat exchanger and condensator 15 located near the bottom of an evaporator 16. An outlet pipe 17 for the condensate is arranged in the bottom of heat exchanger 15; it leads to a holdup tank 18. Tubes 19 and 20 connect the holdup tank 18 with the evaporator 16 and tube 19 connects it also with a scrubber 21. The scrubber is linked to a separator 22, and the latter is connected with the evaporator 16 through pipes 23 and 20. Pipe 24 connects condensator 15 and scrubber 21.

A filter 25 is arranged above and connected with the separator 22. The top of the evaporator 16 is equipped with an exhaust line 26 which leads to a vacuum condenser (not shown) where the steam and any other vapors escaping the evaporator are condensed. A discharge line 27 connects the bottom of the evaporator with inlet pipe 4.

The waste solution is introduced in the form of a spray at the top of the calciner where it passes through zones 5, 6 and 7 for dehydration, calcination and cooling, respectively. The powder suspended in the gas leaving the calciner at its bottom through pipe 8 is separated roughly from the gas in cyclone 9, the solid being discharged through pipe 11. The gas which still contains some fine powder particles is withdrawn at the top of the cyclone and introduced into the top of glass-bag filter 10 where further gas-solid separation is accomplished. The gaseous component is then subjected to a cooling and condensation step by heat exchange in condensator 15; non-condensed fractions leave the evaporator at 26. The cooled condensed liquid is withdrawn through pipe 17 and passed into holdup tank 18. Part of the condensate accumulated in tank 18, preferably about 90% of it, is cycled as cooling medium into evaporator 16, while the rest is introduced into scrubber 21 and utilized for washing the gas. The scrubbed gas leaving the separator is filtered in 25, while the scrubbing liquor is recycled, via pipes 23 and 20, into evaporator 16. Liquid condensed in evaporator 16 is withdrawn at 27 and recycled into the feed line 4 and back into the calciner. Gas noncondensable in the heat exchanger 15 leaves through pipe 24 whence it passes through scrubber 21, etc.

While phosphate and borate anions are the preferred ions for the purpose of converting the calcined waste solution to a glassy water-insoluble material, silicate and mixtures of any of the three can also be used to advantage. The disadvantage of silicate is that a higher processing temperature is needed for the material to melt.

A mixture of borax and sodium silicate, in an equivalence ratio of 2:1 was found to reduce the solubility of the final product of 1.3% of the initial weight as measured in 100 parts of boiling water for one hour; the melting point of the product thus obtained was 850° C. For a waste solution derived from the extraction of uranium, plutonium, etc. with tributyl phosphate, the addition was preferably a mixture of phosphate and borate. All phosphates, borates and silicates that are water-soluble are suitable, including the free acids.

Sugar is preferably added in a quantity ranging from 200 to 400 grams per liter. The wall temperature of the reactor should be maintained at at least 700° C. in order to obtain decomposition of the sugar to carbon.

The process of this invention is usable for all kinds of waste solutions; it has been found particularly advantageous for waste solutions that are derived from extraction processes such as from extraction with methyl isobutyl ketone (hexone) or with tributyl phosphate.

In the following, a few examples are given to illustrate the process of this invention.

Example I shows the advantage of melting the calcined product.

Example I

To a solution simulating a waste solution derived from extraction with tributyl phosphate and of the following composition: $\text{Fe}_2(\text{SO}_4)_3=0.58 \text{ M}$, $\text{Fe}(\text{NO}_3)_3=0.34 \text{ M}$, $\text{Al}(\text{NO}_3)_3=1.02 \text{ M}$, $\text{Na}_2\text{SO}_4=1.20 \text{ M}$, $\text{H}_2\text{SO}_4=0.12 \text{ M}$; 244 grams per liter of phosphoric acid and 144 grams per liter of boric acid were added. This solution was then atomized as described, and a portion of the spray was passed through a 3-inch wide, 3-foot high Vycor tube heated to 500° C. The product leaving the Vycor tube had a bulk density of about 0.1 gram per cubic centimeter. The residence time in the tube was too short, and the droplets consequently were only calcined but not melted. Therefore the material was once more passed through the tube, this time heating it to 900° C. After this, 80% of the calcined product were melted; the all-over bulk density of the product was 0.73 gram per cubic centimeter. Thereafter the product was subjected to screening in order to remove the unmelted portion. The fraction that had been melted had a bulk density of 1.4 grams per cubic centimeter.

Example II

The following example is to illustrate the effect of phosphate on the density of the final product and also the effect of sugar on heat economy of the process.

Three runs were carried out with a synthetic waste solution of the type used in Example I. Calcination at the rate of 0.8 gal./hr. was carried out in a column having a diameter of 8 inches and a height of 10 feet, heated to 325–400° C. at the top and 800° C. in the center; one run was made without phosphate and one was made after 327 grams per liter of phosphoric acid had been added to the solution. The respective densities of the products obtained were 0.42 and 0.82 gram per cubic centimeter.

In a third run, 250 grams of sugar per liter were added together with the phosphate; the product then obtained had a density of 1.05 grams per cubic centimeter.

The required heat input had been reduced by 52% by the addition of sugar when steam atomization was chosen and nitrate was present as an oxidant, while the heat input was reduced by 90% when air or oxygen was introduced with the steam.

The following runs illustrate the effect of additives on the solubility of the solid material. A solution of the following composition— $\text{Fe}(\text{NO}_3)_3=0.35 \text{ M}$,

$\text{Al}(\text{NO}_3)_3=0.10 \text{ M}$

$\text{NaNO}_3=0.60 \text{ M}$, $\text{Cr}(\text{NO}_3)_3=0.09 \text{ M}$, $\text{Ni}(\text{NO}_3)_2=0.09 \text{ M}$, $\text{H}_2\text{SO}_4=0.75 \text{ M}$, was sprayed into the same 8 inch

5

by 10 foot column and heated therein to 900° C. The product was soluble to the extent of 53% in boiling water. Addition of 52 ml. of phosphoric acid per liter of waste solution under the same conditions resulted in a product having a solubility of only 0.55%.

It will be noted that the feed solution of the foregoing examples contains a large quantity of iron. Use of the process of the present invention with such solutions is particularly valuable because iron oxide, formed by the calcination of the iron salts present in the solution, has a tendency to flash off as it is formed and be entrained by the off-gas. This difficulty is avoided by the use of the present invention.

Example III

A further run was carried out with a feed representing aqueous waste from a tributyl phosphate extraction process which was 1.6 M in $\text{Al}(\text{NO}_3)_3$ and 0.5 M in HNO_3 . The 8 inch by 10 foot column was used and heated to 550° C. at the top and 825° C. at the center. Feed at the rate of 1 gal./hour produced a very light powder having a density of 0.11 gm./cc. For a second run the feed was made 1.22 M with $\text{Na}_2\text{B}_4\text{O}_7$ and again calcined at the same temperature and feed rate. Bulk density of the powdered product was 0.70 gm./cc. and this powder could be melted at 800° C. to form a mass of glass with a density of 2.17 gms./cc.

A further test was made on a solution which was 2.20 M in aluminum nitrate, 1.0 M in sodium nitrate and 0.14 M in sodium dichromate. Addition of 440 g./l. of borax and 712 ml./l. of 40° B. sodium silicate gave a glass when heated to 900° C. whose solubility was 4.3%.

The decision as to whether silicate, borate or phosphate should be added and whether this material should be added as the acid or as a salt will depend on the composition of the solution treated. The additive must be one with which a product having a melting point sufficiently low to melt under the conditions of operation of the process is formed and should be selected so as to form a product of maximum insolubility. The above examples illustrate the manner in which this selection should be made.

6

It will be understood that this invention is not to be limited by the details given herein but that it may be modified within the scope of the appended claims.

What is claimed is:

- 5 1. A method of processing radioactive nonacidic waste solutions, derived from the processing of neutron-irradiated uranium, for disposal, comprising adding to said solution a water soluble compound containing an ion selected from the group consisting of phosphate, borate, 10 and silicate ions and mixtures thereof; spraying the solution thus obtained with steam into a space heated at between 325 and 400° C. whereby water evaporates and a powder is formed, heating the powder to melting temperature of between 800 and 1000° C. whereby calcination takes place; and separating water vapor and gaseous substances developed from said calcined product.
- 15 2. The process of claim 1 wherein the waste solution has a high iron content.

References Cited in the file of this patent

UNITED STATES PATENTS

2,308,992 Mertens ----- Jan. 19, 1943

OTHER REFERENCES

- 25 Manowitz et al.: Nuclear Engineering, C.E.P. Symposium Series, No. 12, vol. 50, 1954, pages 144-152; 23-14.5A.
- Durham: AEC Document TiD-7550, June 19-21, 1957 (pp. 8-9).
- 30 Grimmett: AEC Document TiD-7550, June 19-21, 1957 (pp. 38-41).
- Bruce: "Process Chemistry," vol. 2, pp. 424-427, 441, Pergamon Press, N.Y.C., 1958 TK 9350 B7.
- 35 "Proceedings of Second U.N. Conf. on Peaceful Uses of Atomic Energy," vol. 18, Goldman et al., pp. 27-32, Loeding, pp. 56-67, September 1-13, 1958, United Nations, N.Y.
- Empson et al.: AEC Document ORNL-2566, February 17, 1959.
- 40 Hatch and Regan: "Nucleonics," vol. 13, No. 12, pp. 27-29.