

[54] METHOD FOR THE PREPARATION OF CONCENTRATED ANION-DEFICIENT SALT SOLUTIONS

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[58] Field of Search..... 252/301.1 R, 301.1 S

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[57] ABSTRACT

Concentrated anion-deficient salt solutions are prepared of the actinide oxides, PuO2, UO2, UO3, and U3O8 by dissolving one or more oxides in an aqueous solution of thorium nitrate at a concentration of 4 molar or greater and at a temperature of 60° C. or more. Anion-deficient salt solutions of actinide metals so produced are useful as starting materials for the manufacture of ceramic nuclear fuel particles by the sol-gel process.

2 Claims, No Drawings

**METHOD FOR THE PREPARATION OF
CONCENTRATED ANION-DEFICIENT SALT
SOLUTIONS**

Matter enclosed in heavy brackets [] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

This is a division of application Ser. No. 106,922, filed Jan. 15, 1971, now abandoned.

BACKGROUND OF THE INVENTION

The invention relates to the preparation of concentrated anion-deficient salt solutions.

Anion-deficient salt solutions are for instance suitable for the preparation of solid oxide and carbide particles.

For the preparation of spherical particles of ceramic nuclear fuel an anion-deficient solution of uranyl nitrate can successfully be used as a starting material.

In the prior art these solutions have been prepared according to the following methods:

(1) By dissolving UO_3 in concentrated uranyl nitrate solutions,

(2) By the extraction of nitric acid from stoichiometric, possibly slightly acid uranyl nitrate solutions.

These methods show, however, the following drawbacks.

For the purpose of the first method it is necessary to have at one's disposal a UO_3 of such a texture that this substance easily dissolves in the uranyl nitrate solution.

As to the second method it is observed that extraction, whereby nitric acid is withdrawn from a stoichiometric or weakly acid uranyl nitrate solution, can only be applied to dilute uranyl nitrate solutions. Moreover, a special installation is needed for this. After removal of the nitric acid the solution obtained has to be brought to the required degree of concentration, e.g. by evaporation.

The invention aims at giving improved methods for the preparation of an anion-deficient uranyl nitrate solution. Besides it appeared that anion-deficient actinide salt-solutions could be prepared according to several more methods than was formerly possible.

DETAILED DESCRIPTION OF THE INVENTION

According to the invention one or more actinide oxides as PuO_2 , UO_3 or lower uranium oxides than UO_3 are dissolved in a small volume of an acid reacting liquid. The acid reacting liquid consists of a small amount of a strong acid such as a small amount of concentrated HNO_3 , HCl or H_2SO_4 or an aqueous solution of an actinide salt of a strong acid as for instance $UO_2(NO_3)_2$ or $Th(NO_3)_4$.

Mixtures of the above-mentioned liquids can be used too.

With a small amount of liquid is meant that in case of an anion-deficient uranyl nitrate solution the uranium concentration is at least 2 molar.

It is possible to incorporate during the preparation or thereafter small amounts of compounds of other elements in the anion-deficient actinide salt solution in order to improve the properties of nuclear fuel material prepared from this solution.

By other compounds are meant water soluble boron, yttrium, rare earth metals and zirconium compounds.

Examples of the preparation of mixed anion-deficient actinide salt solutions are the dissolving of PuO_2 in uranyl nitrate solution and of UO_3 in thorium nitrate solution.

It has surprisingly been found that anion-deficient solutions of the required nitrate/actinide metal ratio can be obtained by causing lower oxides than UO_3 to react with strong nitric acid, uranyl nitrate solution, thorium nitrate solution or mixtures of these substances in the quantities calculated on the basis of the requirements.

The use of lower uranium oxides than UO_3 has the advantage of better solubility in acid solutions than UO_3 . The difficulty of preparing a UO_3 with a suitable texture namely can be avoided.

Lower uranium oxides than UO_3 are the compounds U_3O_8 and UO_2 . These oxides, along with uranyl nitrate, are the forms in which uranium is obtainable as a basic material. They are also the forms in which uranium is preferably conveyed.

It is therefore of importance to convert these oxides in the easiest possible manner into the solution required for the process to be employed.

The required anion-deficient uranyl nitrate solution may be characterized as follows:

$$\frac{[U]}{[NO_3^-]} \text{ about } 3 \text{ M}$$

$$\frac{[NO_3^-]}{[U]} \text{ about } 1.5$$

It is observed that this uranium concentration is higher than that of the saturated stoichiometric uranyl nitrate solution.

For the preparation of ceramic fissile material a solution of this kind is first mixed with ammonia-liberating agent and then solidified by being dispersed in a phase of sufficiently high temperature, non-miscible with water. With this method it is of great importance to start with highly concentrated uranium solutions.

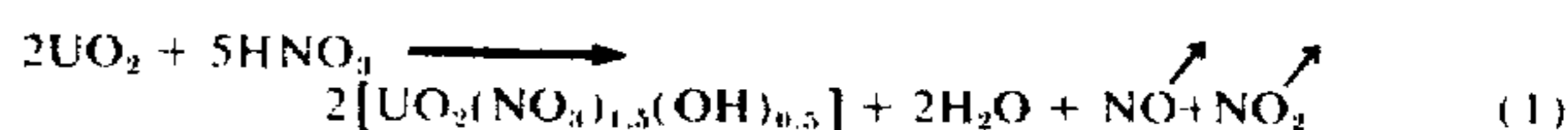
In order to make the rate of solution of the uranium oxide in nitric acid as high as possible, it is important to prepare the U_3O_8 by heating in an oxidizing atmosphere, such as air or oxygen, at temperatures between 600° and 900° C. At these temperatures the most volatile and/or combustible impurities are removed and the texture of the material is still conducive to solution.

Difficultly soluble UO_2 is likewise converted by this thermal processing into easily soluble U_3O_8 .

Very difficultly soluble UO_2 is converted into U_3O_8 by being sintered in air at 700° C. The cubic lattice of UO_2 is thereby changed into the orthorhombic lattice of U_3O_8 . As the molecular volume of U_3O_8 is greater than that of UO_2 , since UO_2 is of higher density than U_3O_8 , the particles are completely crumbled. The high specific surface areas of the U_3O_8 obtained in this way has the effect that it can now be readily dissolved in HNO_3 .

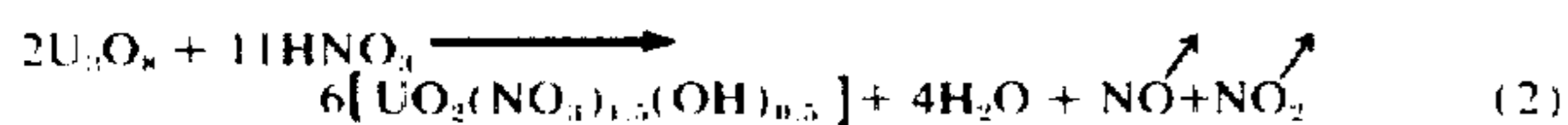
The preparation of U_3O_8 as described above is the ideal method of utilizing waste obtained in the preparation of the ceramic fissile material. For this purpose the waste may consist either of unsintered waste material, possibly containing organic filter material, or of sintered final product composed of UO_2 .

In accordance with the undermentioned gross equations (1) and (2), the quantities of nitric acid used can be determined by calculation.



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-continued



The invention is further elucidated below by reference to a number of examples.

Example I deals with the preparation of an anion-deficient uranyl nitrate solution by dissolving UO₂ powder in nitric acid.

Example II deals with the processing of spherical particles of unsintered UO₃.

Example III deals with the conversion of waste material from spherical particles of UO₂ sintered at high temperatures.

Examples IV relates to the dissolving of U₃O₈ in uranyl nitrate solution.

EXAMPLE I

Degree of enrichment	U ₃ O ₈ , grams	G. mol U ₃ O ₈	ML. HNO ₃ , 14.4M	Mol HNO ₃ /mol U ₃ O ₈	H ₂ O, ml.	Density, g./cm. ³ , 21°C.	[U]		
							Measured	Calculated	[NO ₃ ']/[U]
20%	770.1	0.917	350	5.50	500	1.866	2.82	2.82	1.76
40%	622.3	0.743	270	5.25	300	1.904	2.95	2.97	1.58

A solution test was carried out with natural UO₂ powder in nitric acid with the undermentioned quantities of UO₂ and HNO₃.

Weighed-out

UO₂: 11.4854 g. = 42.5 mmol of UO₂
 HNO₃: 3 × 42.5 = 127.5 mmol of HNO₃

diluted with water to 100 ml. In this example UO₂ was added in portions to the hot (~80° C.) HNO₃ solution.

On account of the fact that during solution in an open beaker some losses of nitric acid occurred, slightly more nitric acid was used than was equivalent to equation (1).

The solution obtained was found to have an NO₃'/U ratio of 1.6.

EXAMPLE II

A quantity of spherical particles of UO₃ was heated slowly in air to 700° C. and then kept at this temperature for another four hours. The following was obtained:

$$249.8 \text{ g. of } U_3O_8, \text{ or } \frac{349.8}{842} \cdot 1000 = 415 \text{ mmol of } U_3O_8$$

This quantity was added in portions to a heated HNO₃ solution consisting of 160 ml. of concentrated HNO₃ (14.4 M) and 258 ml. of water in a beaker. The total volume amounted to 160+258=418 ml., so that after solution the uranium concentration is about 3 M.

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The HNO₃/U₃O₈ ratio used=2300/415≈5.5. According to the gross equation (2) an NO₃'/U ratio ≤ 1.5 may be reckoned with.

Analysis of the solution obtained gave the following results:

$$\frac{[NO_3']}{[U]} = 1.44; [U] = 3.14 \text{ M};$$

density 1.965 g./cm.³ (20.6° C.).

The solution tests were repeated with two quantities of spherical particles of UO₃ with a 20% and 40% enrichment respectively, after they had first been converted into U₃O₈.

The results obtained in this way are set forth below in Table A.

It was observed that by operating in a three-necked flask with a reflux cooler the nitrous vapors had reformed a quantity of HNO₃.

TABLE A

Degree of enrichment	U ₃ O ₈ , grams	G. mol U ₃ O ₈	ML. HNO ₃ , 14.4M	Mol HNO ₃ /mol U ₃ O ₈	H ₂ O, ml.	Density, g./cm. ³ , 21°C.	[U]		
							Measured	Calculated	[NO ₃ ']/[U]
20%	770.1	0.917	350	5.50	500	1.866	2.82	2.82	1.76
40%	622.3	0.743	270	5.25	300	1.904	2.95	2.97	1.58

EXAMPLE III

644.1 grams of spherical particles of UO₂ (sintered at 1400° C. in an atmosphere containing hydrogen), were slowly heated to 750° C. and then kept for four hours at this temperature. In this way 662.5 grams of U₃O₈ were obtained, which could readily be passed into solution according to the method indicated in Example II.

EXAMPLE IV

In this example a quantity of 116 g. of UO₂(NO₃)₂·6H₂O was dissolved in 72 ml. of water and then boiled under reflux with 13.7 g. of U₃O₈ for 2½ hours.

The clear solution obtained had a 2.49 molar content of uranium and an NO₃'/U ratio of 1.62.

What is claimed is:

1. A method for preparing a concentrated anion-deficient actinide salt solution containing at least one actinide oxide selected from the group consisting of PuO₂, UO₂, UO₃ and U₃O₈, said method including dissolving at a temperature of at least 60° C., said [salt] oxide in an aqueous solution of thorium nitrate having a concentration of at least 4 molar.

2. A method for the preparation of a concentrated anion-deficient actinide nitrate solution wherein at least one member selected from the group consisting of uranium dioxide, uranium trioxide and U₃O₈, is dissolved by stirring in a heated thorium nitrate solution of a temperature of at least 60° C., and of a concentration of at least 4 molar, and the solution thus obtained is thereafter diluted with water.

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