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(54) Uranium dioxide pellets

(57) Sintered uranium dioxide pellets composed of particles of size > 50 microns suitable for power reactor use are made by incorporating a small

amount of sulphur into the uranium dioxide before sintering. The increase in grain size achieved results in an improvement in overall efficiency when such pellets are used in a power reactor.

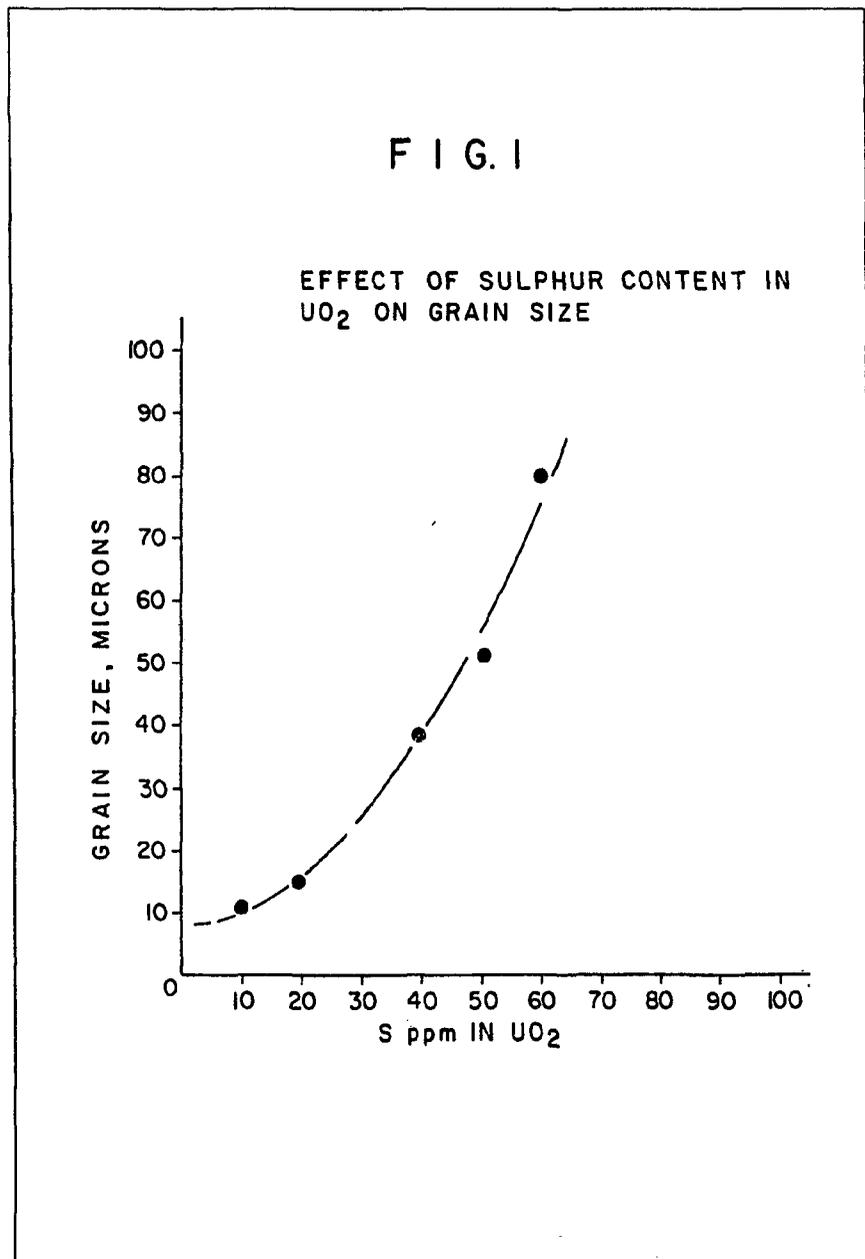
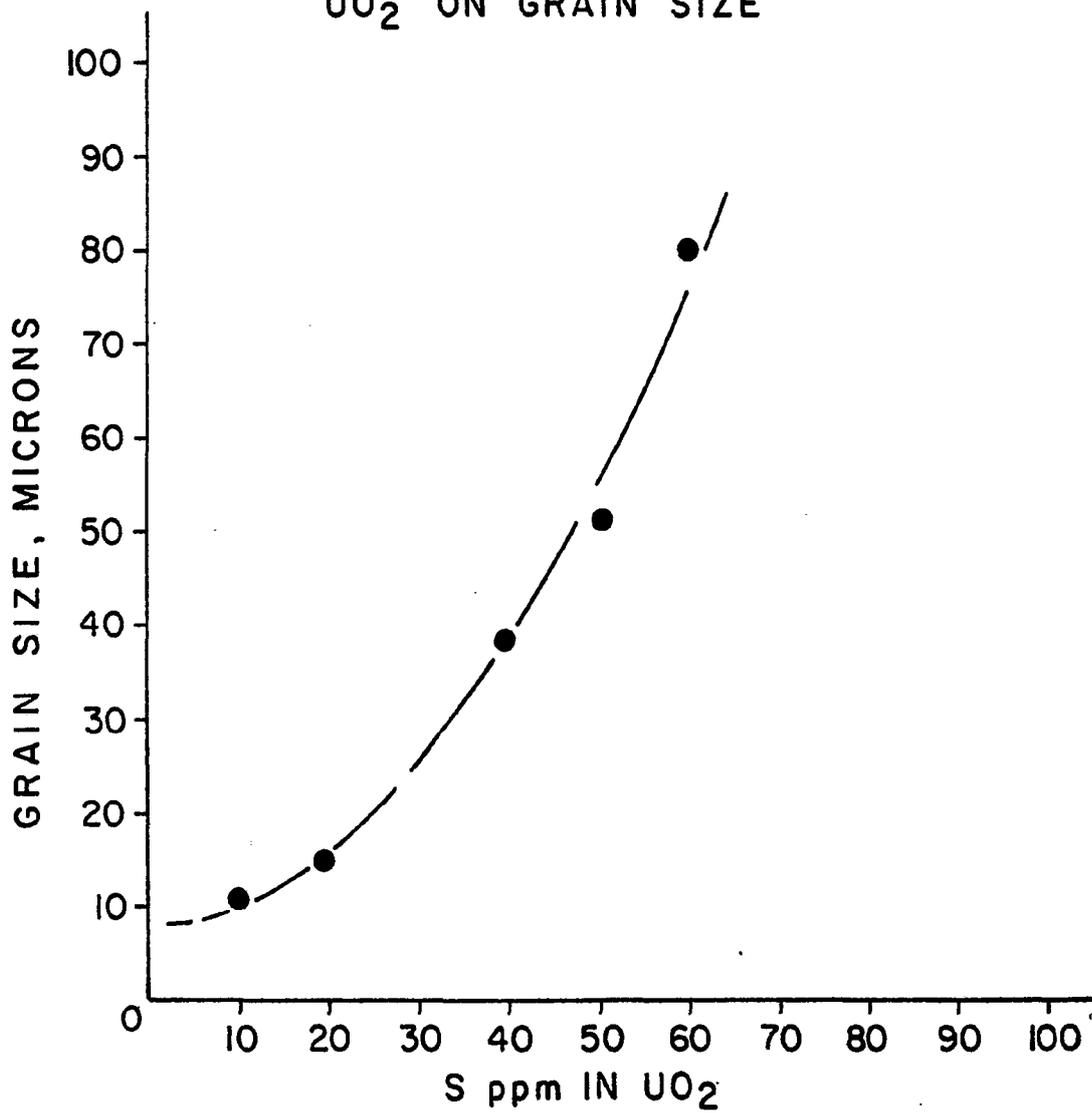


FIG. 1

EFFECT OF SULPHUR CONTENT IN
UO₂ ON GRAIN SIZE

SPECIFICATION

Uranium dioxide pellets

BACKGROUND OF THE INVENTION

This invention relates to the preparation of
 5 uranium dioxide, particularly in the form of pellets
 as used in nuclear reactors for electrical power
 generation purposes.

DESCRIPTION OF THE PRIOR ART

Uranium dioxide, UO_2 , is the fuel most
 10 commonly used in present day nuclear power
 reactors. In its final form, as used in the fuel
 elements, the UO_2 must meet stringent chemical
 and density specifications, which are set by the
 nuclear industry to allow efficient and economical
 15 operation of the power reactors.

The most common method used to obtain the
 high densities required in the pellets used in
 reactor fuel elements, which desirably is greater
 than 95% of the theoretical density for UO_2 in
 20 bulk, is by pressing a UO_2 powder into pellets, and
 then sintering these pellets in a hydrogen
 atmosphere at a temperature of at least $1600^\circ C$.
 Even under these stringent conditions, the UO_2
 powder used generally has a very fine particle size
 25 if pellets which meet the desired density limits are
 to be met.

There are a number of different methods in use
 for producing UO_2 of very fine particle size. The
 method most commonly used is by the hydrogen
 30 reduction of a material commonly called both
 ammonium diuranate, and ammonium uranate,
 which is a solid having a formula approximating to
 $(NH_4)_2U_2O_7$. It is also known by the acronym ADU.
 ADU for this purpose is generally obtained by
 35 precipitation from solution by reacting ammonia,
 or ammonium hydroxide with a solution of uranyl
 nitrate or uranyl fluoride. The ADU formed by this
 procedure has a very fine particle size which
 carries through into the final, sintered, UO_2 pellet.

This process is not without its disadvantages.
 40 An improved process for obtaining UO_2 capable of
 providing sintered pellets of having a higher
 density is described in our South African Patent
 76.1302, issued August, 1977. In this Patent is
 45 described a process for the preparation of fine
 particle size uranium dioxide from a uranium
 trioxide feed comprising the steps of:—

(a) reacting solid uranium trioxide with aqueous
 ammonium nitrate to form an insoluble
 50 ammonium uranate (it is to be noted that although
 described in the same language, this precipitated
 material is chemically different to that mentioned
 above: its formula is generally $6UO_3 \cdot 2NH_3 \cdot 5H_2O$);

(b) neutralizing the thus formed slurry with
 55 ammonium hydroxide to precipitate out as an
 insoluble ammonium uranate the remaining
 dissolved uranium;

(c) recovering the thus formed precipitates in a
 dry state; and

60 (d) reducing the dried precipitate to uranium
 dioxide. The thus obtained dioxide can be
 converted into pellets and sintered, to provide a

pellet having density above 10.64 gm/cc, that is
 better than 97% of the theoretical density of

65 10.96 gm/cc.

However, it is now known that producing a UO_2
 pellet having a high density is not the only
 criterion of relevance, although it is an important
 one. It has now been discovered that the size of
 70 the particles present in such pellets, which can be
 observed and measured, after applying
 appropriate sectioning techniques to a pellet, with
 an optical microscope, has an effect on their
 efficiency, in terms of reactor power output, when
 used as fuel in a nuclear power generating reactor.
 75 It has now been realized that the particle size
 present in the sintered pellets has an effect on the
 rate of loss of fission by-products from the pellet.
 Studies have shown that if the particle size of the
 80 UO_2 present in the sintered pellets could be
 increased to a figure significantly higher than the
 presently larger known particles, which have a size
 of about 25 to 30 microns, then an increase in
 overall power output efficiency should result of the
 order of 5 to 10%.

We have now discovered a simple process
 whereby an acceptable sintered UO_2 pellet may be
 made which not only has a suitably high density,
 and thus is acceptable as a reactor fuel, but also
 90 has an internal particle size considerably larger
 than has hitherto been possible.

The attached single figure shows
 diagrammatically the relationship between grain
 size and green pellet sulphur content.

95 Thus in a first aspect this invention comprises a
 sintered, high density uranium dioxide pellet
 composed of particles having a size in excess of
 50 microns.

In a preferred aspect, this invention comprises a
 100 sintered, high density uranium dioxide pellet
 composed of particles having a size range of from
 50 microns to 1,000 microns.

The process of this invention utilizes most of
 the process steps which are outlined above, and
 disclosed in our South African Patent 76.1302,
 with the addition of one simple, but important
 step. This step is to provide as the initial feed a
 uranium trioxide material containing a known and
 controlled amount of sulphur. By this means, a
 110 uranium dioxide product is obtained which, before
 sintering exhibits a fine particle size which enables
 the preparation of a high density sintered product
 and which exhibits an increase in particle size
 during the sintering procedure.

115 Thus in a second aspect this invention provides
 a process for the preparation of a sintered, high
 density, large particle size uranium dioxide pellet
 which comprises the steps of:

(i) reacting a uranyl nitrate of formula

120 $UO_2(NO_3)_2 \cdot 6H_2O$ with a sulphur source, at a
 temperature of about $300^\circ C$ to about $400^\circ C$ to
 provide a sulphur-containing uranium trioxide;

(ii) reacting the thus obtained modified uranium
 trioxide with ammonium nitrate to form an
 insoluble sulphur-containing ammonium uranate;

125 (iii) neutralizing the thus formed slurry with
 ammonium hydroxide to precipitate out as an

insoluble ammonium uranate the remaining dissolved uranium;

(iv) recovering the thus formed precipitate in the dry state;

5 (v) reducing the dry precipitate to UO_2 and forming it into green pellets; and

(iv) sintered the thus obtained pellets in a hydrogen atmosphere at an elevated temperature.

10 In most of these steps, the conditions are not critical, and the manner in which the various operating parameters may be varied is fully discussed in our South African Patent 76.1302.

15 But in respect of steps (i), (v) and (vi) other considerations apply, since the amount of sulphur, expressed as elemental sulphur, present in the uranium dioxide at the green, unsintered pellet stage has a direct relationship to the particle size obtained in the pellet after sintering. As can be seen from the graphical representation in the attached figure, increase in the sulphur content, expressed as elemental sulphur, in the green pellets increases the particle size in the final pellets, under standardized sintering conditions. Indeed we have found that by the addition of sulphur in this fashion particle sizes in the range of 50 microns up to 1,000 microns are obtainable.

20 The critical point in the process of this invention at which the sulphur content must be controlled is at the green pellet stage. A preferred range of sulphur content, expressed as elemental sulphur, at that point in the process is from about 20 ppm by weight, to about 1,000 ppm by weight. At this level of addition a particle size in the final pellet of up to 1,000 microns can be achieved. Clearly a lower level of sulphur will only provide a particle size toward the lower end of this range: reference is again made to the attached figure.

25 However, the only point in the process at which it is feasible to control the sulphur content is at the beginning, in step (i) as detailed above. It is our experience that in proceeding through steps (i) to (iv), that is from the initial uranyl nitrate feed to an unsintered green pellet, about 75% of the sulphur initially added is lost. It also appears that a scale factor is involved: in small scale laboratory work less sulphur seems to be lost than in larger scale industrial work. Thus it usually will be necessary to establish, by way of experiment, exactly what level of sulphur compound requires to be reacted initially in order to achieve a specified desired level of sulphur in the green pellets, and hence a specified particle size range in the sintered pellets. In our own operations we have found the losses to be of the order of 75% and hence if it is desired to have a sulphur level of 100 ppm in the green unsintered pellets, an addition of 400 ppm requires to be made initially.

30 The form in which the sulphur is added to the uranyl nitrate in step (i) is not critical, and it can be chosen from a wide range of materials. However in its choice, it must also be remembered that some of the sulphur will persist through the sintering stage into the final pellets. Therefore substances containing sulphur which would interfere either with the chemistry leading to the

uranium dioxide used in making the pellets, or in the pressing and sintering operation, or would cause problems when the pellets are used in a reactor, have to be avoided. A reagent which is easily available and meets all of these criteria is sulphuric acid, and hence this is the reagent we prefer to use.

The following general comments apply to all of the subsequent examples.

75 (a) *Uranyl nitrate*

The nuclear grade uranyl nitrate used had the following chemical analysis:

	Impurity	Maximum	Typical
	Ag	1.0	0.1
80	B	0.2	0.15
	Cd	0.2	<0.2
	Cr	10	5
	Cu	50	1
	Fe	30	25
85	Mn	5	<1
	Mo	1	0.5
	Ni	15	5
	P	50	10
	Si	20	<10
90	Th	50	30
	V	30	<10

These levels are in ppm on uranium present basis.

(b) *Ammonium nitrate and ammonia*

95 These were prepared from reagent grade materials. When recycle ammonium nitrate is used both the pH and concentration were adjusted, if need be, by conventional procedures.

(c) *Uranium Dioxide Assessment*

100 The method used was to press the uranium dioxide powder to form green pellets, and then sinter these pellets in a hydrogen atmosphere at a temperature of up to at least 1600°C. The pellets were then suitably sectioned, and the particle size assessed by means of an optical microscope as observed from the face of the section.

(d) *Experimental Procedure*

105 The sulphur additions were carried out by adding a known amount of sulphur compound, generally as sulphuric acid, to uranyl nitrate, and then heating the mixture to a temperature of from about 300°C to about 400°C in order to

decompose the uranyl nitrate to uranium trioxide.

The modified uranium trioxide thus produced was then added to a well agitated vessel containing ammonium nitrate solution at the desired temperature.

The pH of the slurry, recorded during the run, generally dropped to a minimum value in the range 2.5 to 4.0. After the required reaction time, either aqueous (28%) or anhydrous ammonia was added to the slurry. After the ammonia addition, the slurry was usually repulped for 5 to 30 minutes prior to filtering, in order to verify that the pH was not still decreasing.

Filtration was carried out at temperatures up to 70°C, generally above 50°C. After washing with hot water, the cake was dried at 110°C.

Finally, the product was baked, reduced, pelleted, and sintered in conventional production equipment.

Following this procedure a sequence of runs were made in which standardized processing and sintering conditions were used. The only variable changed was the amount of sulphur added. Inspection of the obtained sintered pellets gave the following results. The sulphur was added in step (i) as sulphuric acid.

TABLE 1

Sulphur added, ppm	Sulphur content of green pellets, ppm	Pellet UO ₂ particle size, microns
40	10	11
80	20	15
160	40	38
200	50	41
240	60	80

Other experiments carried out under differing sintering conditions have shown that the presence of from 150 ppm to 300 ppm, of sulphur in the green pellets (measured as elemental sulphur) will provide grain sizes in the sintered pellets of from 500 to 700 microns. Under some sintering conditions grain sizes of up to at least 1,000 microns have been observed. The relevant variable in the sintering process appears to be the rate at which the green pellets are brought to sintering temperature. In the above Table the rate of use was standardized at 200°C per min. The use of a higher rate of use leads to larger final grain sizes when a sulphur source is present in the green pellets.

CLAIMS

1. A sintered, high density, uranium dioxide pellet composed of particles having a size in excess of 50 microns.
2. A pellet according to claim 1 composed of particles having a size range of from about 50 microns to about 1,000 microns.
3. A pellet according to claims 1 or 2, composed of particles having a size range of from about 50 microns to about 100 microns.
4. A pellet according to claims 1, 2 or 3 having a density in excess of 10.64 gm/ml.
5. A process for the preparation of a sintered, high density, large particle size uranium dioxide pellet which comprises the steps of:
 - (i) reacting a uranyl nitrate of formula UO₂(NO₃)₂·6H₂O with a sulphur source, at a temperature of from about 300°C to about 400°C to provide a sulphur containing uranium trioxide;
 - (ii) reacting the thus-obtained modified uranium trioxide with ammonium nitrate to form an insoluble sulphur-containing ammonium uranate;
 - (iii) neutralizing the thus-formed slurry with ammonium hydroxide to precipitate out as an insoluble ammonium uranate the remaining dissolved uranium;
 - (iv) recovering the thus formed precipitates in a dry state;
 - (v) reducing the dry precipitate to UO₂, and forming it into "green" pellets; and
 - (vi) sintering the thus obtained pellets in a hydrogen atmosphere and at an elevated temperature.
6. Process according to claim 5, wherein the green pellets contain more than 200 ppm of a sulphur source, expressed as elemental sulphur.
7. Process according to claim 5 wherein the sulphur source used in step (i) is sulphuric acid.
8. Process according to claim 5 wherein an excess of sulphur source is used in step (i) over and above the level required in the "green" pellets obtained in step (v) thereby to compensate for sulphur losses from the sulphur-containing uranium oxides during steps (i) to (v) inclusive.
9. Process according to claim 5 wherein step (i) is carried out at an elevated temperature.
10. Process according to claim 5 to 7 wherein the step (i) is carried out at a temperature of from about 300°C to about 400°C.
11. Process according to claim 5 wherein in step (vi) the rate at which the green pellets are brought to sintering temperature is adjusted to provide a desired grain size.
12. A sintered, high density uranium dioxide pellet composed of particles of large size, substantially as herein before described.
13. A process for the preparation of a sintered, high density, large particle size uranium dioxide pellet substantially as hereinbefore described.