PARTICLE-SIZE DISTRIBUTION OF AMMONIUM DIURANATE PRECIPITATE

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This investigation was concerned with factors affecting the particle-size distribution of ammonium diuranate precipitate, the primary starting material in the production of uranium dioxide fuel for nuclear power reactors. The ammonium diuranate was prepared in a constant-feed, constant-product removal precipitator by the reaction between a uranyl nitrate solution and ammonium hydroxide. The feed rates were controlled to study the precipitate formed at slurry pH levels of 4, 5, and 6 at each of two uranium concentrations, 50 g and 100 g uranium per liter of uranyl nitrate feed. The temperature was maintained at 50 C. Particle-size distribution was determined by the Andreasen pipet-sedimentation technique using a dilute ammonium hydroxide solution as the suspending medium. The resulting particle-size distributions, found to be log-normal distributions, are shown as cumulative log probability curves.

Uranium dioxide is one of the major fuel materials for nuclear power reactors because of its high density and physical stability at high temperatures. The most important production method at present is the ammonium diuranate (ADU) process which consists chiefly of (a) precipitation of ADU from an aqueous uranium salt solution with aqueous ammonia, and (b) thermal decomposition and reduction to uranium dioxide, which can then be processed into high-density sintered fuel pellets. A generalized flow scheme for the process is shown in Figure 1.

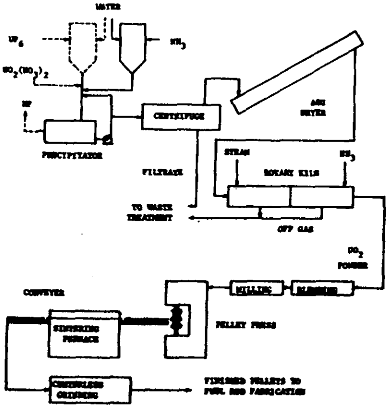

FIGURE 1. Generalized flow scheme of the ADU process. (UF$_6$ feed process = dashed lines; alternate UO$_2$(NO$_3$)$_2$ feed process = dotted lines.

At present most ADU is prepared from a uranium feed produced by hydrolysis of UF$_6$ as it comes from the enrichment process. Some imperfect pellets are recycled by dissolving them in nitric acid to produce a uranyl nitrate solution. With the advent of plutonium recycle as an alternative to the use of enriched uranium, the uranyl nitrate solution produced by fuel reprocessing plants should become the normal feed for the ADU process. For this reason, and because of the relative ease in handling the solutions, this investigation was limited to the ADU process using a uranyl nitrate feed.

In many cases, the ADU precipitate influences the general structure of the final uranium dioxide (1, 2, 3). Powder characteristics, such as surface area, particle size distribution, particle shape, degree of agglomeration, and particle density, have a pronounced effect on the subsequent fabrication process and final product (2, 4). An understanding of the effects of the precipitation conditions on the particle-size distribution could be helpful in maintaining the desired characteristics in the product.

The aim of the present investigation was to determine qualitative relationships between two precipitation variables and particle size distribution.

The overall reaction of interest in the ADU process using a uranyl nitrate feed is:

$$UO_2(NO_3)_2 + NH_3 + H_2O \rightarrow ADU + NH_4NO_3 + H_2O.$$

No simple formula can be given for the

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ADU precipitate; in fact, it is of variable chemical structure as well as variable composition. In the early work on the process it was assumed to be simply ammonium diuranate with the formula $(NH_4)_2U_2O_7$. The abbreviation "ADU" has remained in common use as a designation for the precipitate even though the actual diuranate probably never exists in aqueous solution (3).

Doi and Ito (1) showed, by electron microscopy, that the ADU precipitate usually consists of two or three types of particles. The smallest particles are very thin elementary platelets, approximately 0.1μ thick, but size increases directly with the uranium concentration. Larger particles are formed when the elementary platelets are attracted to each other by weak intermolecular forces and, subsequently, bonded by chemical forces into stable primary aggregates. In addition to these two types of particles, secondary agglomerates may be formed when particles are attracted to each other by weak surface forces. Woolfrey (2) states that, at a uranium concentration of 0.22 mole/l (approximately 52 g/l), larger platelets on the order of 0.2 to 0.5μ are formed and enhanced aggregation takes place to give a much greater size range. Janov et al (3) found that ADU precipitated at pH 3.5 (with 70 g U/l feed) contained numerous aggregates in the size range of 20-24μ, while material precipitated at pH 7.2 contained aggregates of approximately 3μ which, in turn, were weakly connected into chains and secondary clusters. They also found that the size of both the crystallites and aggregates decreased with increasing pH.

METHODS

The apparatus used to determine ADU particle-size distribution is shown in Figure 2. The contactor was initially charged with distilled water. After this water was heated to the desired temperature by pumping it through the loop heated by the electric heater, the uranyl nitrate and ammonium hydroxide feeds were introduced by opening valves to approximate settings. Valves were then manually adjusted to obtain (a) the desired pH and (b) a total feed rate which would achieve the desired holding time in the reactor vessel, i.e., the contactor. The product valve was adjusted to maintain a constant level in the contactor. After flow rates and pH had stabilized for 20-30 min, the valve to the waste tank was closed and a sample was collected.

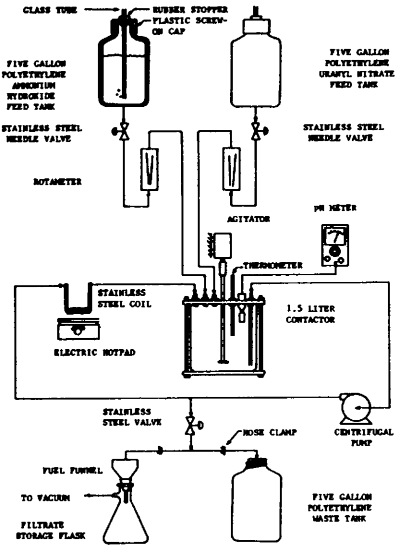

FIGURE 2. Schematic diagram of apparatus used to determine ADU particle-size distribution.

Two methods were used to collect samples for analysis. The first several samples were filtered by vacuum through Whatman #1 filter paper. The filtered precipitate was then allowed to air dry. After drying, the precipitate was chopped with a spatula to about the size of sand grains and then stored in closed jars for later analysis of particle size.

The last few samples were taken by collecting approximately 150 ml of slurry in a millipore-filter funnel lined with 0.45 μ-pore filter paper. Vacuum was applied to remove the liquid from the sample. Without drying, the precipitate was transferred to a small jar and mixed with approximately 100 ml of ammonium hydroxide analysis solution (approximately 10 g NH_3/l). This mixture was then capped and stored for particle-size analysis.

The Andreasen pipet was used to determine particle-size distributions. This method, which is described in some detail in References 5 and 6, essentially determines concentration as a function of time, although the sampling depth varies somewhat throughout the analysis. A 10-ml sample of the suspension is withdrawn by the pipet at various time intervals. Samples are dried and accurately weighed. Results are then compared to the concentration of the initial suspension to determine the weight of the remaining particles. Since the time of sampling and position of the sample are known, the cumulative distribution curve can be calculated.

Samples were drawn at approximately 1, 3.3, 5, 7.5, 10, 15, 20, 52, 83, 167, 325, 504, and 838 min with about 20 sec required to draw each sample. The amount of material left clinging to the walls of the reservoir was found to be quite important for the first three samples. Therefore, after the sample was ejected into the planchet, the material remaining in the reservoir was washed out with 10 ml of distilled water and ejected into an additional planchet for drying and weighing with the main portion of the sample.

RESULTS AND DISCUSSION

The very large particles settled out of suspension so rapidly that they contributed little to the first pipet sample. Use of a higher viscosity fluid in the sedimentation technique would be necessary to analyze the size distribution of very large ADU particles.

Comparison of the screened and unscreened samples indicated that agglomerates produced by drying tend to break up when the powder is resuspended in the ammonia solution. Also, it appeared that the smallest particles formed during grinding and screening must have recombined in solution to give particles above 20μ in radius. A similar recombination of small particles would explain how large particles of about 100μ could be present in solution even after the sample was screened.

Curves of cumulative weight-distribution for most of the samples gave fairly straight lines on semilog paper over much of the particle-size range studied. This type of curve is typical of material which has a log-normal distribution of particles. Herdan (6) states that, although materials which follow a simple normal distribution are relatively rare, they are found chiefly among substances produced by chemical processes, such as condensation and precipitation. Since the ADU is produced by precipitation, a simple normal distribution might be expected. Szego (7), however, states that it is generally accepted that the distribution is log normal.

The data presented here show that, for the range of parameters investigated, the cumulative particle-size distribution of the ADU precipitate can be well represented by a straight line or lines on log-probability paper. Log-probability scales are used because they are most useful in comparing log-normal distributions, which are straight lines in this system (6). Thus, the cumulative distribution can be seen to be log normal. Interestingly, in the case shown as Figure 4, it appears that there are two strata of particle-size distributions, both of which exhibit log-normal behavior.

The effect of an increase in the slurry pH is a narrowing of the overall particle-size distribution. For example, for a pH of 4, as shown in Figure 4, approximately

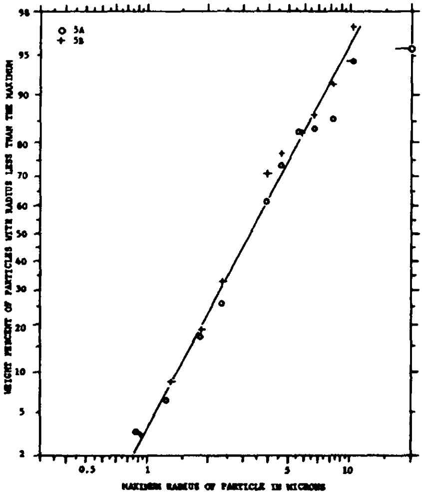

FIGURE 3. Log probability plot of cumulative distribution curves for samples from Run 5 (pH = 5; Temp = 50 C; uranium feed concentration 100 = g/l).

79% of the particles had radii in the 1-10 micron range. For the higher pH of 5, as shown in Figure 3, about 93% of the particles fell in this range.

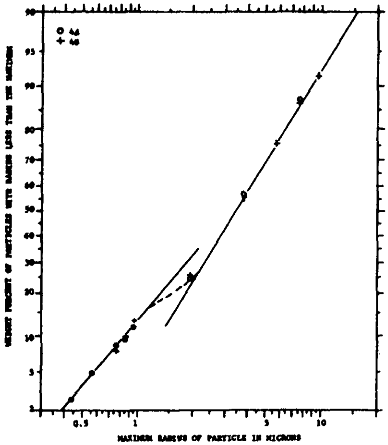

FIGURE 4. Log probability plot of cumulative distribution curves for samples from Run 4 (pH = 4; Temp = 50 C; uranium feed concentration = 100 g/l).

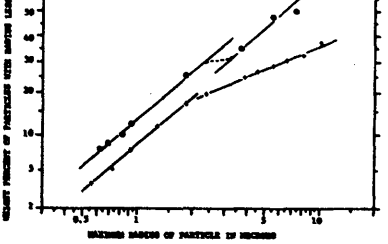

FIGURE 5. Log probability plot of cumulative distribution curves for samples from Run 2 (pH = 5; Temp = 50 C; uranium feed concentration 50 g/l.

The effect of an increase in the uranium concentration of the uranyl nitrate feed was also a narrowing of the particle-size distribution. Although the data are more scattered for the runs which were made at the lower uranium concentration, the trend is clear. Figure 5 shows that only about 30-45% of the particles were in 1-10μ range for a uranium-feed concentration one-half that of the run shown in Figure 3. Both of these distributions are for pH 5.

Thus, the effect of changing the pH at which the precipitation occurred did not seem to be as great as that of changing the uranium concentration. This result is the opposite of that reported by Reinhart (8), but he investigated a different range of pH values. In the present study, both the feed concentration and the pH values were chosen to be in the range of current commercial practice.

CONCLUSIONS

The following conclusions were reached. The cumulative particle-size distribution of the ADU precipitate exhibited log-normal behavior. An increase in the slurry pH narrows the distribution. An increase in the uranium concentration of the feed also narrows the particle-size distribution. The uranium concentration, at least for the range of values investigated, has more effect on the distribution than does the pH.

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