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THE PREPARATION AND CALCINATION OF AMMONIUM URANATES - A LITERATURE SURVEY

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J.L. WOOLFREY

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ABSTRACT

The preparation and calcination of ammonium uranates is reviewed. Topics covered include the preparation of ammonium uranates by precipitation or solid state reaction; the effects of preparation conditions upon the composition, structure, morphology, surface area, and filtration of ammonium uranates; the thermal decomposition and reduction of ammonium uranates; and the effect of calcination conditions on the physical properties of the resultant powder.

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1. INTRODUCTION

In the past ten years the development of nuclear power reactors has led to an increase in the importance of uranium dioxide as a nuclear fuel. The fabrication of UO_2 fuel elements generally involves preparation of an inorganic hexavalent uranium compound, calcination to UO_3 and/or reduction to sinterable UO_2 powder, followed by cold pressing and sintering of fuel pellets(1). Considerable evidence shows that the sintering characteristics of ceramic powders, such as UO_2, are determined largely by their preparative history.

Starting materials that have been used for the preparation of UO_2 include(1,2):

Ammonium uranates.

Higher uranium oxides and their hydrates.

Uranyl nitrate, oxalate and peroxide.

Uranyl acetate, benzoate, tannate and quinolinate.

Production techniques generally use uranyl nitrate as the starting material for the preparation of UO_2 and this is subsequently denitrated thermally, or chemically by addition of ammonia to precipitate ammonium uranates. Powders made by the thermal denitration route normally have poor sintering characteristics and are used to produce uranium fluoride feed for diffusion plants. The most sinterable grades of commercially produced UO_2 are prepared by the ammonium uranate route. This process forms the basis of the UO_2 fuel element technologies developed in U.K., U.S.A., Canada, France, India, Denmark and Sweden.

Many reports have been published about the nature, preparation and calcination of ammonium uranates. However, a great deal of confusion has been generated by the conflicting nature of many of the results. This report critically reviews the most important results and attempts to clarify the reasons why disagreement exists. It also indicates fruitful areas for future investigation.

2. PREPARATION OF AMMONIUM URANATES

Ammonium uranates have been formed in the solid state by reaction of gaseous or liquid ammonia with uranyl nitrate hexahydrate(3) and hydrated UO_3(4,5), and the reaction of UO_3 with a solution of water and ammonia(6). These methods have no commercial importance but are of value as preparative techniques for research related to the composition and structure of ammonium uranates.

Ammonium uranates are precipitated by the reaction of a uranyl solution, normally nitrate, with ammonia or a donor compound containing ammonia. Ammonia may be added

(i) directly as gaseous or liquid ammonia or aqueous ammonium hydroxide$^{(1)}$,

(ii) by an ammonia donor such as urea$^{(4,7)}$, ammonium carbonate$^{(8)}$, or ammonium sulphate$^{(4,9)}$.

Most commercially produced ammonium uranates are prepared by method (i) but Sweden uses urea, which has the advantage that precipitation occurs homogeneously throughout the solution. The A.A.E.C. Research Establishment is at present interested in the former route and this method of precipitation will be the only one reviewed in this paper.

Precipitation of ammonium uranates by the ammonia route has been carried out by:

(i) A batch process, when complete precipitation is accomplished at a given pH, or precipitation is followed by conditioning of the precipitate with excess ammonia to ensure complete precipitation.

(ii) Continuous precipitation, which normally involves at least two stages; either precipitation at a given pH followed by conditioning, or partial precipitation at a low pH followed by complete precipitation at a higher pH.

The following variables have been found to affect the precipitation of ammonium uranates:

Use of gaseous or liquid NH_3 or aqueous NH_4 OH.

Uranium concentration.

Ammonia concentration.

Addition sequence.

Precipitation temperature.

Effect of excess ammonia.

Degree of agitation.

Ageing of precipitate.

and such dependent variables as

pH.

Rate of precipitation.

The effect of these variables on the physical properties of the precipitate will be discussed in Section 4. It is difficult to assess the quantitative effects of these variables since the precipitation of ammonium uranates occurs by heterogeneous nucleation and the design of the apparatus has a major influence. However, qualitative trends are evident in the results reported in the literature.

3. THE COMPOSITION AND STRUCTURE OF AMMONIUM URANATES

3.1 Composition

Among the various compositions reported for uranates(10) are the following: M_2UO_4, $M_2U_2O_7$, $M_2U_3O_{10}$, $M_2U_4O_{13}$, $M_2U_6O_{19}$, $M_2U_7O_{22}$ and $M_2U_8O_{25}$, where M is a monovalent cation (e.g. NH_4^+, Na^+, K^+). These compositions fit the general formula $M_2U_xO_{3x+1}$ suggesting the series:

$M-O-UO_2-O-M$	normal uranate
$M-O-UO_2-O-UO_2-O-M$	diuranate
$M-O-UO_2-O...UO_2-O...UO_2-O-M$	polyuranate

Such a stoichiometric series of compounds would imply that the ammonia is present as bonded NH_4^+ ions in ammonium uranates.

Other workers(4,5) postulate the existence of a series of UO_3-hydrate-ammoniates with the general formula $UO_3 . xNH_3 . (2-x)H_2O$, where part or all of the ammonia exists in the lattice as coordinated NH_3 groups. They believe that other series of $UO_3-H_2O-NH_3$ compounds may also occur depending on whether the system being investigated is liquid or dry and whether or not nitrate is present.

Addition of ammonia to a solution of uranyl nitrate causes formation of a precipitate which was originally believed to be ammonium diuranate(11), $(NH_4)_2U_2O_7$, often referred to as ADU in the technical literature. However, recent investigations have revealed the complex nature of such a precipitate. According to the data in the literature, the mole ratio UO_3/NH_3 of the precipitates isolated from uranyl nitrate solutions may vary within the range 4.0 to 0.7 depending on the conditions of precipitation (Figure 1). It is difficult to compare results because of non-equilibrium conditions and possible hydrolysis of the precipitate during washing with water. The possibility of hydrolysis of the precipitate was reported by Ewing in 1956(12) but this effect has often been ignored. The analytical data of the precipitates are also difficult to interpret, as in all cases appreciable but not reproducible amounts of nitrate are retained which cannot be completely removed by washing with water or alcohol. Washing with alcohol appears desirable since it does not cause the drastic changes in composition that occur during water washing.

In an effort to prepare nitrate-free precipitates, Cordfunke(6) investigated the ternary system NH_3-UO_3-H_2O by reacting UO_3 with various concentrations of water and ammonia at 40°C until equilibrium was reached. Chemical and X-ray analysis revealed the formation of four compounds (Table 1). Compound I contained some ammonia. He found that Compound II was the only uranate stable in the presence of moist air. The others decomposed such that,

Compound IV $\rightarrow$ III $\rightarrow$ II .

The strong resemblance between the X-ray patterns of uranates precipitated from uranyl nitrate solution and that of $UO_3.2H_2O$ led Hermans(4,5) to investigate the possibility of replacing H_2O with ammonia in the lattice of the dihydrate. He found that the reaction of $UO_3.2H_2O$ with liquid ammonia produced a compound whose composition could be varied within the limits $UO_3.\frac{2}{3}NH_3.\frac{4}{3}H_2O$ to $UO_3.\frac{1}{2}NH_3.\frac{3}{2}H_2O$, while still retaining the same hexagonal structure. These chemical compositions were essentially the same as those found by Cordfunke(6). Hermans also found that the reaction of gaseous ammonia with $UO_3.2H_2O$ produced a series of compounds with an upper limit of $UO_3.\frac{4}{5}NH_3.\frac{6}{5}H_2O$.

3.2 Structure

The structures reported for ammonium uranates prepared by several different methods(4,5,13,14,15) are collated in Table 2. The structures consist essentially of hexagonal or pseudohexagonal layers of composition $UO_2(O_2)_\alpha$ with the additional O and N atoms of water and ammonia between these layers(4,14). A model for the oxygen bonding was proposed by comparison with an α-UO_3 structure(14), which has since been shown to be incorrect(16). Thus the proposed oxygen configuration around the uranium atoms could well be incorrect. The resemblance between the structures of uranates and $UO_3.2H_2O$ is striking(4,5,14). The orthorhombic lattices in the series are pseudohexagonal and differences between the lattices can be explained by minor distortion and shrinkage of one lattice. This structural similarity can be traced to the existence of sub-lattices which are almost identical in the various compounds(14). Reflections from the heavy uranium atoms, which are situated approximately at the corners of the sub-cells, dominate the X-ray powder diffraction patterns and nothing can be deduced concerning the positions of the light atoms.

Although there is some discrepancy concerning lattice parameters, the compounds isolated by Cordfunke(6,14) and Hermans(4,5) were essentially the same. However, Cordfunke found two limiting hexagonal compounds (Types III and IV) separated by a two-phase region, while Hermans concluded that a continuous region existed over these limits. The results of Jakes et al.(13) indicate that the Type IV compound can contain considerable excess ammonia without any apparent major change in the observed X-ray powder diffraction patterns. Examination of ammonium uranates by infra-red spectrophotometry (Stuart and Whateley, A.A.E.C. - to be published) has shown that the U=O stretching frequency ν_{U-O} exhibits a significant and continuous variation with UO_3/NH_3 ratio down to 1.43 (covering Types I to IV). No evidence of the frequency splitting which would normally be associated with mixtures of compounds could be found. This suggests that a single phase region exists within these composition limits. More precise structural analysis using single crystal diffraction methods is required to resolve this problem.

Disagreement also exists as to the exact nature of these compounds : whether or not they are real uranates, with all the ammonia bound as NH_4^+, or UO_3-hydrate-ammoniates with the ammonia present as coordinated NH_3 groups. Cordfunke(5) considers that his compounds are real uranates while Hermans(4,5) considers that they are UO_3-hydrate-ammoniates. Chemical and X-ray analysis alone does not seem capable of resolving this problem as results indicate that the compounds can contain large amounts of excess ammonia, without any major effect on the X-ray structures. Precise infra-red and NMR analysis may help with this problem. Deane(17) investigated several specimens of ADU using infra-red analysis and found no evidence of the presence of NH_4^+ bonding. Whateley (A.A.E.C. - unpublished results) feels that this interpretation has been confused by the presence of nitrate impurity. In regions normally associated with ammonia bonding, the spectra show a similarity to those of many simple ammonium salts. Recent French infra-red experiments have also been interpreted in terms of NH_4^+ bonding(18). DTA and gas evolution analyses, which will be discussed in Section 5, show that the ammonia is not evolved from the uranates below 250°C and this indicates that the ammonia is strongly bound. The argument for the existence of UO_3-hydrate-ammoniates is based on the rapid and reversible exchange of NH_3 with H_2O at room temperature(4) and the strong resemblance between the X-ray patterns of the uranates and $UO_3.2H_2O$(5). However, neither of these is a really conclusive argument against the existence of uranates. The majority of direct evidence would appear to favour the interpretation that they are real uranates. Hermans(4) feels that a different series of compounds may be formed depending on the starting material, the presence of nitrate, and whether the system is liquid or dry. More closely controlled experiments are needed to resolve this question.

4. THE EFFECT OF PREPARATION CONDITIONS ON THE PROPERTIES OF AMMONIUM URANATES

The effects of the process variables listed in Section 2 on the composition, structure, morphology, surface area and filtration rates of the ammonium uranates will now be reviewed.

4.1 Composition

Although numerous experiments have been carried out to determine the effect of process variables on the composition of the product, it is difficult to compare results because of non-equilibrium conditions for some experiments, presence of residual nitrate and hydrolysis of the precipitate during washing.

4.1.1 Batch precipitation

Numerous workers(4,5,6,11,13,18,19,20,21) have studied the reaction between uranyl nitrate solution and ammonia by means of potentiometric and conductimetric titration measurements associated with chemical analysis to determine the products formed. In aqueous solution, all positively charged ions tend to associate with water (hydrolysis) and a large proportion also associate with other coordinating groups to form complex ions (polymerisation) linked through the formation of hydroxyl bridges. The initial UO_2^{2+} ions are hydrolysed to form polynuclear complexes(4,21) of the type $U_2O_5^{2+}$, $U_3O_8^{2+}$, $U_3O_8(OH)^+$ or $UO_2[(OH)_2UO_2]_n^{2+}$. Conflicting results are reported in the literature and the confusion is associated with the complex nature of the titration curves. Hermans(4) found that several independent phenomena may influence the shape of these curves:

(1) The slow rate at which the hydrolytic-polymeric reaction takes place leads to non-equilibrium conditions.

(2) The hydrolytic-polymeric phenomena may be different depending whether hydrolysis takes place by dilution or by increasing the alkali content.

(3) The occurrence of different compounds and transformations between them may cause a decrease in pH even when no true hydrolytic reaction takes place.

He concluded from the results of his investigation that it is difficult to obtain reproducible and meaningful results and that equilibrium cannot be reached during a titration at room temperature.

Cordfunke(6) attempted to achieve equilibrium by heating at 40°C for 1 to 2 weeks. Figure 2 shows the curve in which the pH of the saturated solution is plotted against the NH_3/UO_3 molar ratio of the initial solution. The equilibrium curve is obviously different from that obtained by direct titration (dotted line). Under equilibrium conditions, precipitation started at pH = 3.5 and was completed at pH = 4. Hermans(4) found that the pH for initial precipitation was strongly dependent upon the uranyl nitrate concentration of the solution and the rate of addition of the ammonia. This possibly explains why such a range of pH values has been reported in the literature.

Ippolitova(20) observed inflection points in the conductimetric and potentiometric titration curves which indicated that five different products may be formed during precipitation. The calculated compositions corresponded to $UO_2(OH)_2$, $(NH_4)_2U_7O_{22}$, $(NH_4)_2U_4O_{13}$, $(NH_4)_2U_2O_7$ and $(NH_4)_2UO_4$. Other authors have also reported indications of the formation of $UO_2(OH)_2$(11), $(NH_4)_2U_7O_{22}$(22,23), $(NH_4)_2U_4O_{13}$(22,23), $(NH_4)_2U_2O_7$(11) and $(NH_4)_2UO_4$(11). However, it appears to be impossible to isolate many of these single compounds from solution and the inflections may be due to metastable complex ion formation(18).

The results obtained at equilibrium are of interest for explaining the stable composition of the uranates. X-ray analysis showed that the precipitates isolated by Cordfunke(6) had diffraction patterns identical with those of the following compounds as listed in Table 1:

pH			Type
< 3.5	(incomplete precipitation)	→	I
4 to 7		→	II
> 7		→	III with some II

A rapid conversion of Type III to II occurred when the precipitate was washed in water. Deptula(21) found compositions similar to Types II and III over similar pH ranges but he postulates more precise formulae. He found that if ammonia is added slowly and the solution allowed to stand until an equilibrium pH is established, the compound has the composition $[(NH_4)_2O]_3.[UO_3.H_2O]_{20}.13H_2O$ (i.e. Type II) which reacts further to form $[(NH_4)_2O]_5.[UO_3.H_2O]_{20}.7H_2O$ (i.e. Type III). A rapid addition of ammonia led to the formation of a precipitate with the composition $[(NH_4)_2O]_{2.5}.[UO_3.H_2O]_{20}.14H_2O$ (i.e. $UO_3.\frac{1}{4}NH_3.\frac{7}{4}H_2O$) which reacts with excess ammonia to form $[(NH_4)_2O]_5.[UO_3.H_2O]_{20}.7H_2O$. Ippolitova(20) also found a composition equivalent to the Type II over a pH range of 8 to 9. At a lower pH of 5 to 7 he found a composition close to $(NH_4)_2U_7O_{22}$ and at pH > 9 close to diuranate. There were significant deviations from stoichiometry in both cases. However, the compositions could be suspect since he washed the products with NH_4NO_3 solution and recent work at this Research Establishment (W. Stuart - unpublished results) has shown that this can substantially alter the composition of $UO_3.2H_2O$ by exchange reactions. Notz et al.$^{(24)}$ concluded that ADU was probably a mixture of hydrated polyuranates.

$$(\text{anion-}UO_2\text{-}O\text{-}UO_2\text{-anion}).xH_2O$$

where the anions are 52 per cent hydroxyl, 39 per cent oxyammonium and 9 per cent unreplaced nitrate.

Hermans$^{(4)}$ investigated the reaction using several different methods;

(i) Slow addition of aqueous ammonia to a uranyl nitrate solution.

(ii) Very rapid addition of the ammonia.

(iii) Slow simultaneous addition of uranyl nitrate and gaseous ammonia to a uranyl nitrate-ammonia system of the right pH in a ratio such that the pH was kept constant.

(iv) Slow reaction of gaseous ammonia with a uranyl nitrate solution.

By X-ray analysis he distinguished three products which he designated α, β and γ, with transition points at a pH around 3 and 9 respectively (Figure 1). The product β corresponded to a Type II composition. The α-compound had a mole ratio UO_3/NH_3 of 3.3 and γ-compound often contained excess ammonia. He found that the transition $\beta \rightleftarrows \gamma$ was reversible in the mother liquor and depended solely on pH, whereas under nitrate-free conditions the reaction $\gamma \rightarrow \beta$ seemed to be irreversible. Unlike Deptula$^{(21)}$, he found no influence of the method of precipitation on the types of products obtained.

The results of Jakes et al.$^{(13)}$ are rather different from those of other workers (Figure 1). Comparison shows that their samples contained much more ammonia than recorded elsewhere, which they attributed to the strength of the solutions used in the precipitation. However, X-ray analysis (Table 3) showed that the compounds had diffraction patterns similar to those of the products formed by Cordfunke$^{(6)}$. Certain deviations from Cordfunke's results can be observed at 60°C; for instance, Type II was not found, whereas Type I existed even at a pH = 5 and contained some ammonia. The composition at pH = 9 is very close to that of the diuranate but no change in structure from a Type IV compound was found. At 40°C and pH = 9, a compound with a UO_3/NH_3 mole ratio of 0.75 was formed but the X-ray analysis revealed only a Type IV compound. This would indicate that large excesses of ammonia were present compared with the compounds prepared by Cordfunke(6).

Brusset and Dao(18) found that only uranates formed with a large excess of ammonia had a well defined composition ($UO_3.\frac{1}{2}NH_3.\frac{3}{2}H_2O$). For lower ammonia mixtures, the chemical compositions varied considerably.

4.1.2 Continuous precipitation

Little information is contained in the literature concerning the composition of the products formed during continuous precipitation. Experiments at the A.A.E.C. (Woolfrey - unpublished results) have shown that using gaseous ammonia, the following compounds were formed at 40°C:

pH		Type
4.5	→	II
6-7.5	→	III and IV
8.6	→	IV

The UO_3/NH_3 ratios are shown on Figure 1.

4.2 Morphology

The characteristics of a given powder, such as UO_2, are determined by its method of preparation and subsequent thermal treatment. Powder characteristics such as surface area, particle shape, particle size distribution, degree of agglomeration and particle density have a pronounced effect on subsequent fabrication processes. Since these characteristics are basically inherited from the precursor material(25), the effect of preparation variables on the characteristics of the precursor powder are of great interest.

4.2.1 Particle shape and size

Doi and Ito(26) showed by electron microscopy that the elementary uranate particles are usually very thin platelets. These platelets are normally attracted to each other, plane to plane, by weak intermolecular forces and are subsequently bonded by chemical forces, leading to the formation of stable primary aggregates. Secondary agglomerates may be formed during drying when particles and/or aggregates are held together by relatively weak surface forces. The agglomerates normally can be broken up by handling or dispersion techniques. Confusion is generated in the literature by referring to any of these as the 'particle size' without further clarification.

The same authors(26) found that when the uranium concentration of the nitrate solution was low (0.004 mole/litre) the length of the platelets remained small and uniform (0.1 to 0.2 μm), and they formed small aggregates of uniform size (0.2 to 0.3 μm). A higher uranium concentration (0.22 mole/litre) gave rise to larger platelets (0.2 to 0.5 μm) and enhanced aggregation, with a much wider size range. Considerable agglomeration must take place during drying of the precipitate since the size distribution measured by a sedimentation technique(26,27) showed that at least 50 to 80 per cent of the powder had a 'particle' size greater than 2 μm.

For batch precipitation with NH_4OH, the literature indicates that a low uranium concentration (below 300 g/litre), high or excess NH_4OH concentration, increased temperature, and rapid precipitation all contribute to the development of a precipitate of small 'particle' size(28,29,30). Reinhart(31) using a four factor analysis of variance , investigated the effects of precipitation variables on 'particle' size of uranates for continuous precipitation with NH_4OH, and the results are given in Table 4. He found that pH exerted the strongest effect but precipitation temperature and uranium concentration have strong secondary effects, particularly in combination with each other and with pH. When gaseous NH_3 is used as the precipitant, the 'particle' size is uniformly smaller(28,32) and is relatively insensitive to precipitation conditions(28).

4.2.2 Particle density

The effects of precipitation conditions on the apparent density of uranates, measured by the displacement of liquid carbon tetrachloride or trichlorethylene(8,33,34), have been reported in the literature. These values would represent the apparent density of the aggregates since the liquid molecules cannot penetrate the smallest pores.

Dembinski(33) found that for the batch production of uranates with NH_4OH, both uranyl nitrate concentration and rate of precipitation affected the density of the particles as measured by carbon tetrachloride (Figure 3). The density of uranates precipitated under equilibrium conditions decreases with increase in uranium concentration. However, if precipitation is carried out rapidly, no effect is evident. Presumably in the latter case, precipitation is controlled not by the uranium concentration but by the supersaturation of the solution with ammonia, which was the same for all uranium concentrations. Increasing the temperature of precipitation decreases particle density. Clayton(8) and Galkin(32) reported that precipitation with NH_4OH produced denser particles than those precipitated by gaseous ammonia (Figure 3).

Vuillemey(34) found that the density was insensitive to precipitation conditions for uranates prepared by continuous precipitation with NH_4OH. He states that the apparent density of the uranates tends to increase with final pH.

4.3 Surface Area

Determination of the surface area of ammonium uranates is itself a problem. The range of values reported in the literature can be attributed to:

(i) The measured value of the surface area depends upon the method used: conventional BET, continuous flow BET, or permeability(13).

(ii) The uranate surface must be cleaned of other gases at below 50°C(13,20,35) since water of crystallisation is lost above this temperature(20).

(iii) There is some difficulty in obtaining a stable uranate surface under vacuum at such low temperatures(13).

(iv) Curved plots result when krypton adsorption is measured over the normal range of relative pressures (0.05 to 0.35) and analysed by the BET equation(35).

Jakes(13,36) found a rather complicated dependence of the BET surface area on the final pH for batch precipitation using NH_4OH (Figure 4). The minimum at $pH \approx 6$ would appear to be related to the structural change in the precipitate from orthorombic to hexagonal (see Table 2). Clayton(8) and Dembinski(33) found significantly different values of surface area for precipitation in the region of $pH \approx 8$ to 8.5 (Figure 4). This may be due to differences in the size of apparatus, the stirring conditions and the method of surface area measurement.

Dembinski(33) found that the specific surface area of uranates decreased with increasing uranyl nitrate concentration but increased with increasing temperature and rate of precipitation (Figure 5). Jakes(13) similarly found that an increased rate of precipitation resulted in an increased surface area. He also found that the rate of stirring had an effect. Clayton(8) found that precipitation with gaseous ammonia resulted in a significant increase in surface area (Figure 5).

Vuillemey(34) investigated the continuous precipitation of uranates with NH_4OH and found that only the final pH of precipitation had any systematic influence on surface area, an increase being observed with increasing pH (see Table 5). It is interesting to note that two-stage precipitation caused a reduction in surface area for a given final pH.

Since surface area is to some extent a measure of 'particle' size, it is interesting to note that the effects of changes in precipitation conditions upon 'particle' size (Section 4.2.1) are confirmed by the parallel but inverse variation in surface areas recorded above.

4.4 Filtration

Reinhart's results(37) show that the filtration rate of uranate precipitates prepared by continuous precipitation with NH_4OH is strongly dependent on the final pH of the solution (Figure 6). The highest filtration rate was observed at a pH = 5.7. He also found that the filtration rates were 10 to 50 times greater than for batch-precipitated uranates under similar conditions. Curtis(38) observed a similar dependence over a much wider pH range (Table 6), and the results indicate that, for a constant pH (=6) and feed acidity, increased uranium concentration leads to enhanced filterability. Deptula(21,39) found that for batch precipitation, rapid precipitation leads to a poorly filterable precipitate.

4.5 Discussion

The results reviewed in Section 4.1 lead to a rather confused picture of the exact nature of ammonium uranates. Results indicate the occurrence of UO_3-hydrate (I), $UO_3.\frac{1}{3}NH_3.\frac{5}{3}H_2O$(II), and $UO_3.\frac{1}{2}NH_3.\frac{3}{2}H_2O$(III) during precipitation from uranyl nitrate solution. With a very large excess of ammonia, $UO_3.\frac{2}{3}NH_3.\frac{4}{3}H_2O$(IV) is also formed. Commercial ADU is generally a mixture of some or all of these. This is possibly due to the fact that the initial compound to be precipitated at a low pH (3 to 3.5) is $UO_3.xH_2O$ (containing small amounts of ammonia) which is subsequently converted to Compound II at a higher pH. Further conversion of Compound II to III and IV is reported to be very slow. Thus the chemical composition and compounds observed depend on the rate of conversion. It is also important to note that although pH is often reported in the literature as if it is a primary variable in the precipitation, it is in fact a dependent variable. This, and the problems of analysis and hydrolysis of the precipitate (Section 3.1), has helped to contribute to the confusion in the literature concerning the composition of the material precipitated at a given pH.

The effect of an increase in particular precipitation variables on the physical properties of ammonium uranate precipitates are collated in Table 7, for both batch and continuous precipitation. With batch precipitation, virtually all the variables have major effects on the physical properties of the precipitates. However, with continuous precipitation, pH is the most important variable, with uranium concentration and temperature having important secondary effects. Two-stage precipitation(34) is often favoured owing to flexibility in control of composition and uniformity of precipitate. Many of the correlations are based on very limited information and more precise experiments are required, using multi-factor analysis of variance to reveal the interaction effects between variables.

5. CALCINATION

The calcination of ammonium uranates to form UO_2 may be effected via three different routes:

$$\begin{tikzcd}
\text{'ADU'} \arrow[rr] \arrow[d] & & UO_2 \\
UO_3 \arrow[urr] \arrow[r] & U_3O_8 \arrow[ur] &
\end{tikzcd}$$

Two different processes may be involved,

(a) thermal decomposition,

(b) reduction.

5.1 Thermal Decomposition

The thermal decomposition of ammonium uranates has been studied by a number of authors but their results are not in complete agreement.

5.1.1 Composition

The composition of the compounds formed during the decomposition of ammonium uranates in air or an inert gas has been studied by various authors using DTA, TGA, chemical and X-ray analysis(20,24,40,41,42). The DTA and TGA show four corresponding thermal deflections associated with weight losses:

(i) Endothermic deflections in region 50 to 250°C;

(ii) Exothermic deflections in region 250 to 350°C;

(iii) Exothermic deflections in region 350 to 450°C;

(iv) Endothermic deflections in region 500 to 600°C.

Dehydration of ammonium uranates starts at 20°C(20) and proceeds up to 200°C, which is obviously associated with the first endothermic deflection. Interpretation of inflections in the curves between 200 and 300°C is complicated by the presence of variable amounts of nitrate impurity and the fact that all the ammonia may not be bound as NH_4^+. Notz(24) claims that the first exothermic peak (ii) corresponds mainly to nitrate loss with a small amount of ammonia. However, Ippolitova(20) considers that this peak is associated with detachment of an NH_4^+ ion which takes place in two stages. Notz(24) carried out a similar experiment with nitrate-free uranate, prepared from sulphate solution, and found only one exotherm, at 415°C. It would thus appear that the first exotherm is associated with nitrate removal. The origin of the heat generated is not definitely known but Notz(24) suggests that it may result from heat of polymerisation or the exothermic decomposition of evolved ammonium nitrate.

The second exotherm from 350 to 450°C is mainly associated with the evolution of the remaining ammonia during the decomposition, to form UO_3(20,24,43). Between 450 and 500°C a minor exotherm is associated with the formation of some U_3O_8 due to the auto-catalytic reduction of the UO_3 with evolved ammonia(20,24), a process which is known to be exothermic. Ippolitova(20) and Landspersky(43) also associate this effect with the formation of a solid solution between UO_3 and U_3O_8 to give $UO_{2.9}$. The final endothermic deflection represents decomposition of the remaining UO_3 into U_3O_8 at about 600°C in air, and decomposition terminates at 640°C.

Two types of UO_3, amorphous UO_3(A) and crystalline β-UO_3, have been reported in the literature(43,44,45) as being formed during the decomposition of ammonium uranates. Hoekstra(46) observed the formation of the UO_3(A) at temperatures much lower than those observed for the formation of the crystalline forms. Landspersky(43) found the formation of both UO_3(A) and β-UO_3 at a temperature of 200°C. He also found that the rate of heating had an effect on the type of UO_3 formed(44). Slow heating (1 degC/min) gave UO_3(A) while rapid heating (10° to 100 degC/min) gave a mixture of β-UO_3 + UO_3(A). Hoekstra(46) found that UO_3(A) could not be transformed into any crystalline modification at normal pressures without loss of oxygen below the stoichiometric ratio O/U = 3. He found the following decomposition sequence:

$$UO_3(A) \xrightarrow{450°C} UO_{2.9} \xrightarrow{550°C} U_3O_8 \quad .$$

At 525°C the decomposition of β-UO_3 to give U_3O_8 was also observed. A further complication can result from the fact that in a moist atmosphere the initial mixture of UO_3(A) + β-UO_3 may become hydrated to form $UO_3.\frac{4}{5}H_2O$(44). This compound is not completely dehydrated until 350 to 400°C is reached. The decomposition product is UO_3(A).

Until the UO_3 or U_3O_8 phase is formed, X-ray powder diffraction techniques do not provide much additional information about the composition of the initial decomposition products, owing to the continuity of the sub-lattice of uranium atoms. The diffraction data(24) shows a slight lattice contraction and disordering as decomposition proceeds, which could be a natural result of the removal of anions.

5.1.2 Morphology - particle size and shape

Doi and Ito(26) observed that the calcination of ammonium uranates in air at 400°C did not essentially modify the shape of the precipitate except for the development of minute holes in the elementary platelets. Samples of β-UO_3 prepared at 500°C showed a similar retention of shape(45) and had a crystallite size, measured by X-ray line broadening, of about 150 Å. Poorly crystalline samples exhibited crystallite growth, increasing to about 300 Å in about 12 hours. Calcination above 600°C modified the shape of the precipitate by microsintering(26), leading to neck formation and accelerated growth of the U_3O_8 particles. Imris(27) found that calcination of U_3O_8 in the temperature range 600 to 1000°C, produced smaller aggregates than those of the original uranates, presumably because of disruption of aggregates during decomposition. The size distribution, measured by a sedimentation technique, increased in breadth up to 700°C, narrowed at 800°C and then increased again above 850°C, owing to the balance between particle growth and shrinkage of the aggregate from internal sintering. The narrowest distribution was obtained for calcination at 800°C.

5.1.3 Morphology - surface area

The surface area of calcined ammonium uranates increases rapidly between 300 and 400°C(36,40,43) (Figure 7). This would appear to be associated with the formation of UO_3 during decomposition (Section 5.1.1). The effects of microsintering, leading to a relative reduction in surface area, can be seen above 400°C. Increases in time or temperature produce a greater reduction in surface area(43). The effect of the high surface area, leading to microsintering at lower temperatures, can also be seen in Figure 7. Surface area decreased by a factor of 8 to 10 if hydration-dehydration took place during calcination(44). This appeared to be due to crystal growth of the UO_3-hydrate.

The surface area of U_3O_8 is clearly determined by microsintering effects(36) (Figure 7). The method of precipitation of the ammonium uranates also affects the U_3O_8 surface area.

Changes in surface area above 600°C, (Figure 7) reflect inversely the variation in 'particle' size reported by Imris(27). The stable surface area values between 700 and 800°C would appear to be associated with the narrowing of the size distribution. Below 450°C, the rapid increase in surface area is due to the formation of holes in the elementary platelets(26).

5.2 Reduction

Gaseous reduction to produce UO_2 can be accomplished with H_2,H_2/N_2 mixtures or CO by:

(i) direct reduction of ammonium uranates;

(ii) reduction of UO_3 or U_3O_8 produced by the initial decomposition of ammonium uranates.

5.2.1 Composition

Ammonium uranates can be directly reduced to UO_2 by heating in hydrogen(8,26,33, 36,40,47,48) or carbon monoxide(8,47). However, basic information about the reduction process is very limited. Huntington(40) investigated the reduction in hydrogen which appeared to be a three-stage process:

$$\text{'ADU'} \longrightarrow UO_{2.56} \longrightarrow UO_{2.5} \longrightarrow UO_2 \quad .$$

The rate curves appeared to be linear between the steps and the rate of conversion of $UO_{2.56}$ to $UO_{2.5}$ was the slowest step in the process (Table 8). He found that the rate of reduction increased up to 590°C but there was only a relatively small increase above 480°C. Auto-reduction of ammonium uranates can be achieved on a laboratory scale from the hydrogen produced by the dissociation of ammonia released during the calcination to U_3O_8(49). The temperature of reaction must be above 450°C for appreciable ammonia dissociation and U_3O_8 reduction to occur. The optimum reduction temperature was found to be about 700°C.

Huntington(40) also investigated the reduction in hydrogen of ammonium uranates which had been calcined at 538°C to give a mixture of UO_3 and U_3O_8. The reduction curves were similar to those observed for direct reduction but only exhibited a two-stage process:

$$\text{calcined 'ADU'} \longrightarrow UO_{2.56} \longrightarrow UO_2 \quad .$$

In the primary reduction stage to $UO_{2.56}$, the rate of direct reduction was greater than that for the calcined material; beyond this point the calcined material reduced faster (Table 8). The difference between the rates of the primary stage of reduction to $UO_{2.56}$ was contrary to what would be expected on the basis of surface area values. At 400°C, the calcined material had a specific surface area of 15 m^2/g compared to 7 m^2/g for the directly reduced material, yet the latter exhibited faster reduction rates.

Information concerning the reduction of UO_3 and U_3O_8 is available in the literature, but the results have proved conflicting(1). The reduction kinetics appear linear, indicating a surface reaction, and the reported activation energy for reduction varies between 26 and 39 kcal/mole. De Marco and Mendel(50) observed a two-stage process during the reduction of high surface area UO_3 in the temperature range 300 to 400°C:

$$UO_3 \longrightarrow UO_{2.56} \longrightarrow UO_2 \quad .$$

However, Notz and Mendel(51) observed a three-stage process for the reduction of UO_3 with specific surface areas in the range 2 to 5 m^2/g at temperatures of 450 to 550°C.

$$UO_3 \longrightarrow U_3O_{8+y} \longrightarrow U_3O_{8-x} \longrightarrow UO_2 \quad ,$$

where U_3O_{8+y} and U_3O_{8-x} refer to the upper and lower limits of the U_3O_8 phase. These results are in agreement with those of Huntington(40) who observed a similar two-stage process for the reduction of high surface area material calcined to give UO_3 or U_3O_8 and a three-stage process for the low surface area uranates which had been directly reduced. The U_3O_{8-x} phase has a lower limiting O/U ratio of 2.55, over the temperature range 400 to 600°C(52). It would appear that direct reduction of ammonium uranates occurs via U_3O_8 with the initial rate change at $UO_{2.56}$ being associated with the phase boundary of U_3O_{8-x}.

Kuhlman(53) found that NH_3 was less effective in reducing UO_3 than either H_2 or a 3 to 1 molar mixture of H_2/N_2.

5.2.2 Morphology - particle size and shape

Doi and Ito(26) observed that the shape of the precipitate persists throughout calcination and/or reduction at temperatures below 600°C. Clayton(8), Landspersky(43 and Anderson(47) found that to a first approximation, the X-ray crystallite size of the resultant UO_2 depended upon the maximum temperature of calcination or reduction rather than on the method of preparation. Reduction with CO tended to give a finer powder for a given set of calcination conditions(44). The size distribution of agglomerates in UO_2 powders varies from 4 to 90 μm(1,26,27). Imris et al.(27), using a sedimentation technique, made a detailed study on the effect of reduction conditions on agglomeration. They observed the following results for reduction with hydrogen:

(i) For direct reduction, the size distribution of the UO_2 up to 50 μm was directly related to that of the ammonium uranate and the reduction temperature. Above this size, the UO_2 was finer and the size distributions were different.

(ii) The size distribution of the UO_2 prepared via U_3O_8 depended on the temperature at which the U_3O_8 was calcined.

(iii) A relationship existed between the size distribution of the U_3O_8 calcined at 650°C and the UO_2 prepared from it. No relationship existed for calcination above this temperature, and for U_3O_8 calcined below 650°C the subsequent UO_2 was finer than the U_3O_8.

(iv) The UO_2 prepared via U_3O_8 contained a larger proportion of smaller particles than that prepared by direct reduction. It also had larger crystallites and smaller agglomerates than powder produced by direct reduction, which produced small crystallites and large agglomerated particles. The U_3O_8 route gave a single-peaked (4 to 12 μm) Gaussian size distribution, while direct reduction gave a double-peaked (12 to 60 μm up to 900°C) distribution.

(v) Small UO_2 agglomerates consisted of large crystallites and vice versa.

(vi) The smallest size distribution range of agglomerates was prepared by calcination of U_3O_8 at 800°C and reduction at 700°C.

5.2.3 Morphology - surface area

In general, the surface area of UO_2 powders depends both on the surface area of the materials from which they are prepared and on their thermal history.

Direct reduction of ammonium uranates with hydrogen below 650°C led to a slight increase (8 per cent) in surface area(47). However, reduction above 800°C resulted in a rapid loss in surface area due to sintering of the UO_2 powder(8,47). Clayton(8) and Belle and Lustman(54) reported that no dependence between the surface area of the uranate and that of the resultant UO_2 could be found. However, Jakes(13) reported a linear dependence between the two surface areas, measured by permeability. This apparent discrepancy would appear to arise from the fact that the powders of Clayton(8) and Belle(54) were reduced at high temperatures for long periods of time and thus microsintering would have a modifying effect on such a relationship.

Hydrogen reduction of UO_3 and U_3O_8 produced by decomposition of ammonium uranate leads to a slight increase in surface area at temperatures below 600°C(8,47). However, above 600°C, decreases occur owing to sintering of the powders(8,36,46). The increase in surface area below 600°C was associated with 'particle' breakdown due to the difference in crystal structure and density of U_3O_8 and UO_2. Greater 'particle' breakdown occurred at lower temperatures because of lower mobility in the solids and because strains caused by the phase transformation are less easily annealed out at these lower temperatures. The surface area of the UO_2 depended on the surface area of the higher oxide from which it had been prepared(8,46). The relation for UO_3(43) and U_3O_8(36) is shown in Figure 8. A complication arises in Landspersky's results(43) as the surface area of the UO_3 was measured by permeability but that of the UO_2 by BET. However, the results indicate that a relationship between the surface areas does exist. The kink and change in slope of the U_3O_8 curve occurs for powders calcined at greater than 700°C and is probably associated with sintering of the powders. The UO_2 powders prepared by pre-calcination of ammonium uranates to UO_3/U_3O_8 in the temperature range 400 to 600°C normally had surface areas twice as large as those prepared by direct reduction over the same temperature range(36,43).

The surface area of the UO_2 powder can be modified by subsequent thermal treatment.

(i) Oxidation of UO_2 to U_3O_8 below 300°C can cause a considerable increase in surface area(8,55,56) and subsequent reduction at 500°C may increase this surface area by a factor of 10(57).

(ii) High-temperature sintering of the powder reduces the surface area. Reduction of the surface area begins at a lower temperature in vacuum or argon (600°C) than in hydrogen (800°C)(58).

5.2.4 Morphology - particle density

In general, the real density of the UO_2 powder, corrected for excess oxygen, depends on the density of the parent oxide, UO_3 or U_3O_8(8,46), but not upon that of the ammonium uranate(8) for the direct reduction process. The density is independent of the reduction temperature up to 1200°C. Reduction with CO instead of H_2 results in measurably higher densities under similar reduction conditions(46).

5.3 Discussion

Although the decomposition and reduction reactions of ammonium uranates have been investigated by many workers, the results do not give a clear picture of the compounds formed or any real analysis of the kinetics of the processes, and little information is available concerning the effects of uranate composition or calcination atmosphere. This is largely due to the technological nature of much of the work.

Similarly, the work on powder morphology and inter-relationships with the properties of precursor compounds, has not produced any really penetrating analysis of the problem. No attempt has been reported of determination of orientation relationships during decomposition and reduction, and hot-stage electron microscopy could help to resolve this problem. Determination of the inter-relationships between the crystallite, particle, and aggregate size and size distribution, and correlation with surface area and density has not produced many definite results because the techniques used (such as sedimentation analysis, electron and optical microscopy, BET and permeability) have often been applied in isolation. A programme is required in which all of these are applied to the same material. The modifying effects of sintering of the calcined powder upon such inter-relationships has often been ignored and this has caused confusion in the interpretation of results and in attempting to decide whether or not a simple relationship exists.

6. CONCLUSIONS

The major points which arise in the previous sections may be summarised as follows:

1. Multi-stage continuous precipitation of ADU is favoured over batch process for reasons of control and economics.

2. Gaseous ammonia would appear to have advantages over ammonium hydroxide as the precipitant.

3. Uranate powders with a high surface area and small particle size can be prepared by using a high $pH^{(\approx 7)}$ a low uranium concentration (< 0.1 mole/litre), a high temperature ($> 60°C$), a high rate of precipitation and gaseous ammonia as the precipitant. Such powders give maximum flexibility in the reduction process for producing sinterable UO_2.

4. Commercial ADU is normally a mixture of $UO_3.\frac{1}{3}NH_3.\frac{5}{3}H_2O$, $UO_3.\frac{1}{2}NH_3.\frac{3}{2}H_2O$, and perhaps some $UO_3.\frac{2}{3}NH_3.\frac{4}{3}H_2O$, depending on the precipitation conditions. The majority of direct evidence favours the interpretation that these compounds are real uranates.

5. The surface area, 'particle size' and density of the ammonium uranate powders is strongly dependent on the precipitation conditions, namely pH, uranium concentration, temperature, rate of precipitation, and nature of the precipitant.

6. Calcination of ammonium uranates for form UO_2 can be effected via three different routes involving thermal decomposition and/or reduction with hydrogen or carbon monoxide.

$$\begin{tikzcd}
\text{'ADU'} \arrow[r] \arrow[d] & UO_2 \\
UO_3 \arrow[ur] \arrow[r] & U_3O_8 \arrow[u]
\end{tikzcd}$$

7. Thermal decomposition of ammonium uranates up to 400°C leads to a rapid increase in surface area, but above this temperature sintering of the particles leads to a relative reduction.

8. Direct reduction of ammonium uranates with hydrogen involves a three-stage process,

$$\text{'ADU'} \longrightarrow UO_{2.56} \longrightarrow UO_{2.5} \longrightarrow UO_2 \quad ,$$

while calcined uranates (UO_3/U_3O_8) involve a two-stage process,

$$\text{Calcined 'ADU' } (UO_3/U_3O_8) \longrightarrow UO_{2.56} \longrightarrow UO_2 \quad .$$

The reduction kinetics appear to be linear between the steps.

9. The UO_2 powders prepared by pre-calcination to UO_3/U_3O_8 in the temperature range 400 to 600°C and reduction in the same range, normally have surface areas twice as large as those prepared by direct reduction over the same temperature range.

10. For both reduction routes, the 'particle' size and surface area of the UO_2 is directly related to the 'particle' size and surface area of the precursor uranate or oxide. These relationships can be substantially modified by sintering of the particles and this has caused some confusion in the interpretation of results.

11. Crystallite size of the UO_2 depends on the maximum temperature of calcination or reduction rather than on the method of preparation.

12. The real density of the UO_2 powder depends on the density of the precursor oxide in the calcination-reduction process but not on that of the uranate in the direct-reduction process.

13. There is a need for more detailed scientific studies in many of these areas, using a variety of sophisticated techniques in parallel.

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TABLE 1

COMPOSITION OF THE COMPOUNDS IN THE TERNARY SYSTEM NH_3-UO_3-H_2O - after Cordfunke(6)

Type	Composition
I	$UO_3.2H_2O$
II	$UO_3.\frac{1}{3}NH_3.\frac{5}{3}H_2O$
III	$UO_3.\frac{1}{2}NH_3.\frac{3}{2}H_2O$
IV	$UO_3.\frac{2}{3}NH_3.\frac{4}{3}H_2O$

TABLE 2

STRUCTURE OF AMMONIUM URANATES

Reference	Method of Preparation	Composition	Structure	Cell Dimensions		
				a	b	c
14	UO_3-H_2O-NH_3 solution	$\beta UO_3.2H_2O$ (I)	orthorhombic	13.977	16.696	14.672
		$UO_3.\frac{1}{3}NH_3.\frac{5}{3}H_2O$ (II)	orthorhombic	7.220	12.198	15.072
		$UO_3.\frac{1}{2}NH_3.\frac{3}{2}H_2O$ (III)	hexagonal	14.087	-	14.494
		$UO_3.\frac{2}{3}NH_3.\frac{4}{3}H_2O$ (IV)	hexagonal	4.031	-	14.58
15		$UO_3.\frac{1}{4}NH_3.\frac{7}{4}H_2O$ (II)	orthorhombic	7.16	12.21	14.06
4,5	$UO_3.2H_2O$-liquid ammonia	$UO_3.\frac{1}{2}NH_3.\frac{3}{2}H_2O$	hexagonal	4.09	-	7.50
		$UO_3.\frac{2}{3}NH_3.\frac{4}{3}H_2O$	hexagonal	4.03	-	7.12
	$UO_3.2H_2O$-gaseous ammonia	$UO_3.\frac{4}{5}NH_3.\frac{6}{5}H_2O$	hexagonal	4.03	-	7.07
13	ppt$^{\underline{n}}$ from uranyl nitrate solution with NH_4OH at 40°C pH3	I	orthorhombic			
	4	I	orthorhombic			
	5	mixture-mainly I				
	6	not identified				
	7	III	hexagonal			
	8	IV	hexagonal			
	9	IV	hexagonal			
	60°C pH3	I	orthorhombic			
	4	I	orthorhombic			
	5	II	orthorhombic			
	6	not identified				
	7	III	hexagonal			
	8	IV	hexagonal			
	9	IV	hexagonal			

TABLE 3

EFFECT OF pH AND TEMPERATURE ON THE COMPOSITION OF URANATES PRECIPITATED FROM URANYL NITRATE SOLUTION WITH NH_4OH - after Jakes et al.(13)

pH	Type of Compound Formed	
	60°C	40°C
3	I	I
4	I	I
5	Mixture-mainly I	II
6	Mixture-not identified	Mixture-not identified
7	III	III
8	IV	IV
9	IV	IV

TABLE 4

RANK OF PRECIPITATION VARIABLES AS TO EFFECT ON PARTICLE SIZE - after Reinhart(31)

Classification of Effect	Variable or Combination of Variables	Averaged Effect of Increasing Variables on Particle Size (% < 10 μm)
Major	P	+ 49
Moderate	UP	20
	TP	18
	TUP	18
	U	15
	NP	15
	NUP	14
	TU	12
	TNP	12
	T	10
Small	TNU	8
	TN	5
	N	NS
	NU	NS

P = pH of precipitation

T = Temperature of slurry

U = Uranium concentration of uranyl nitrate solution

N = Concentration of ammonia solution

NS = Not significant

TABLE 5

EFFECT OF FINAL pH OF PRECIPITATION ON THE SURFACE AREA OF AMMONIUM URANATES PREPARED BY CONTINUOUS PRECIPITATION WITH NH_4OH - after Vuillemey$^{(34)}$

	Final pH	Specific Surface Area (m^2/g)
Single-stage precipitation	7.6	10.9
	9.0	14.8
Two-stage precipitation	7.6	6.9
	8.9	12.8

TABLE 6

EFFECT OF FINAL pH OF PRECIPITATION ON THE FILTERABILITY OF AMMONIUM URANATES PREPARED BY CONTINUOUS PRECIPITATION WITH NH_4OH - after Curtis[38]

Feed Solution		Control pH	Relative Filtration Rate M^*
U Concentration (g/litre)	H^+ Concentration (N)		
75	0.5	4	12.6
75	0.5	6	6.4
75	0.5	6	6.0
75	0.5	10	1.25
140	0.5	6	10.8
200	0.5	6	11.6
235	2.5	7	2.4

$$^*M = A\,(zp\,x\,c/\eta r T)^{\frac{1}{2}}$$

where A = surface area of filter

x = fraction of drum surface immersed

M = solid mass per unit time

T = time of drum revolution

r = filtration resistance

c = solids concentration

p = pressure (or vacuum)

η = viscosity

TABLE 7

EFFECT OF AN INCREASE IN PARTICULAR PRECIPITATION VARIABLES ON THE PROPERTIES OF AMMONIUM URANATES

Batch Precipitation

Precipitation Variables	Particle Size	Particle Density	Surface Area	Filtration Rate
pH	decrease	-	increase	decrease
U concentration	increase	decrease	decrease	-
Temperature	decrease	decrease	increase	-
Rate of precipitation	decrease	no effect	increase	decrease
Agitation	-	-	had effect	-
Gaseous NH_3 instead of NH_4OH	decrease	decrease	increase	-

Continuous Precipitation

Precipitation Variables	Particle Size	Particle Density	Surface Area	Filtration Rate
pH	decrease	increase	increase	decrease
U concentration	decrease	-	-	increase
Temperature	decrease	-	-	-
Rate of precipitation	-	-	-	-
Agitation	-	-	-	-
Gaseous NH_3 instead of NH_4OH	-	-	-	-

TABLE 8

REDUCTION OF AMMONIUM URANATES WITH HYDROGEN - after Huntington(40)

	Dried 145°C			Calcined 538°C	
Temperature of reduction °(C)	457	428	397	426	397
Starting composition-I	$UO_{2.88}$	$UO_{2.96}$	$UO_{3.00}$	$UO_{2.72}$	$UO_{2.72}$
Composition of primary break in reduction curve-II	$UO_{2.57}$	$UO_{2.57}$	$UO_{2.57}$	$UO_{2.61}$	$UO_{2.56}$
Composition of secondary break in reduction curve-III	$UO_{2.51}$	$UO_{2.47}$	$UO_{2.47}$	-	-
Rate I → II (mg/sec)	0.427	0.300	0.155	0.161	0.083
II → III	0.119	0.065	0.024	-	-
III → UO_2	0.189	0.086	0.030	-	-
II → UO_2	-	-	-	0.089	0.036

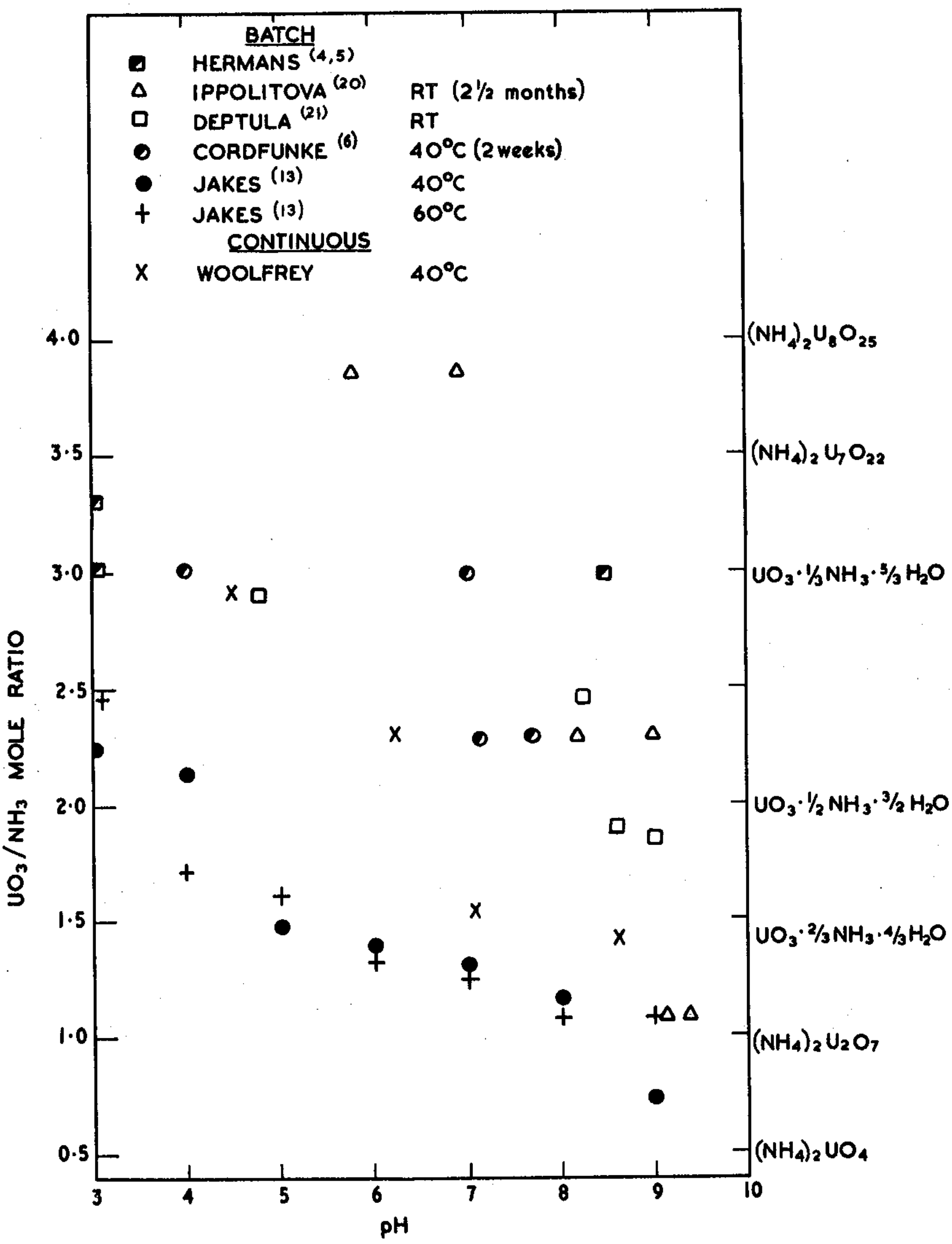

FIGURE 1. DEPENDENCE OF THE COMPOSITION OF AMMONIUM URANATES ON THE FINAL pH OF PRECIPITATION

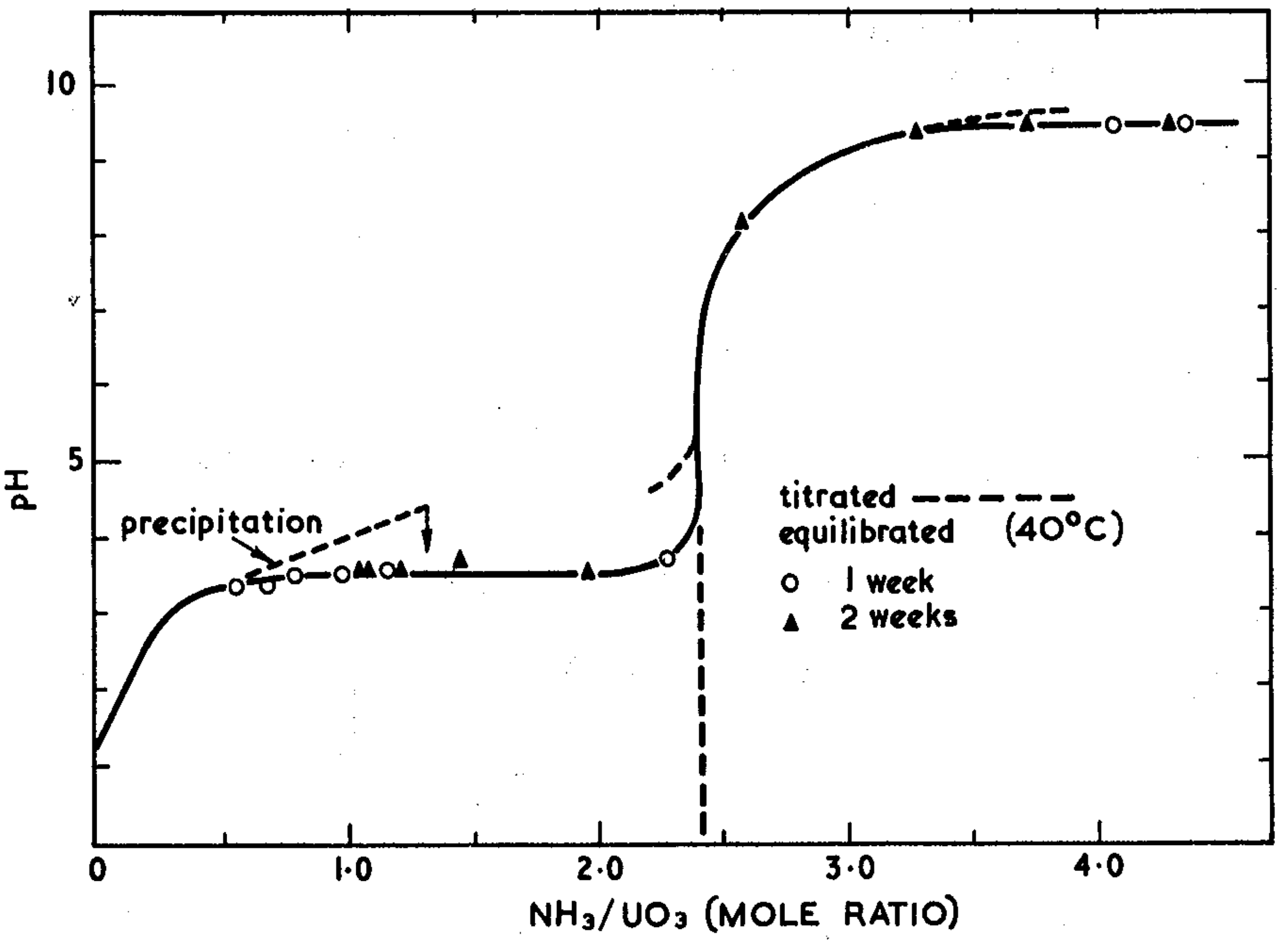

FIGURE 2. pH-CURVE OBTAINED BY ADDITION OF AMMONIA TO URANYL NITRATE SOLUTION - AFTER CORDFUNKE(6)

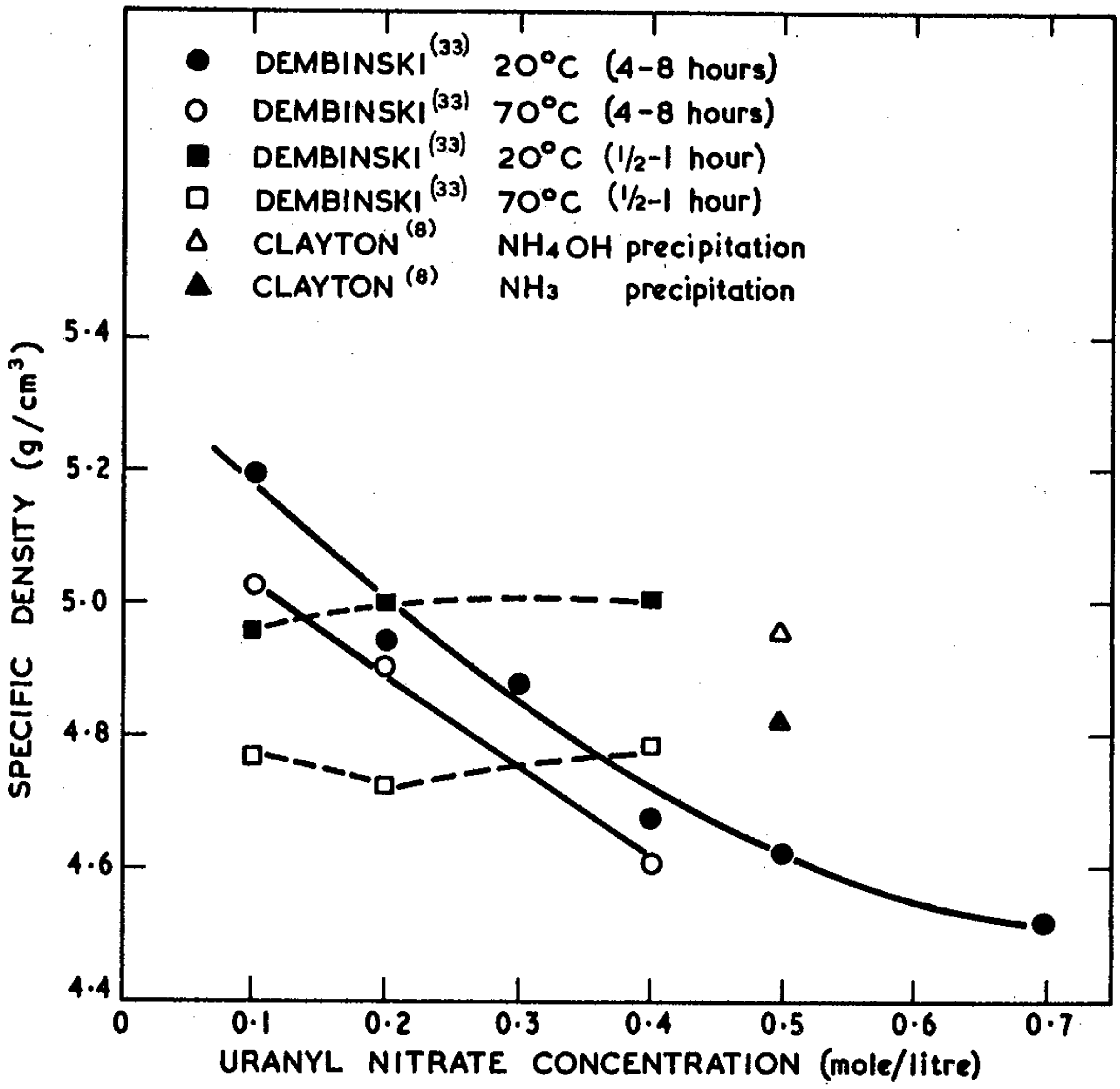

FIGURE 3. EFFECT OF URANYL NITRATE CONCENTRATION ON THE DENSITY OF AMMONIUM URANATES

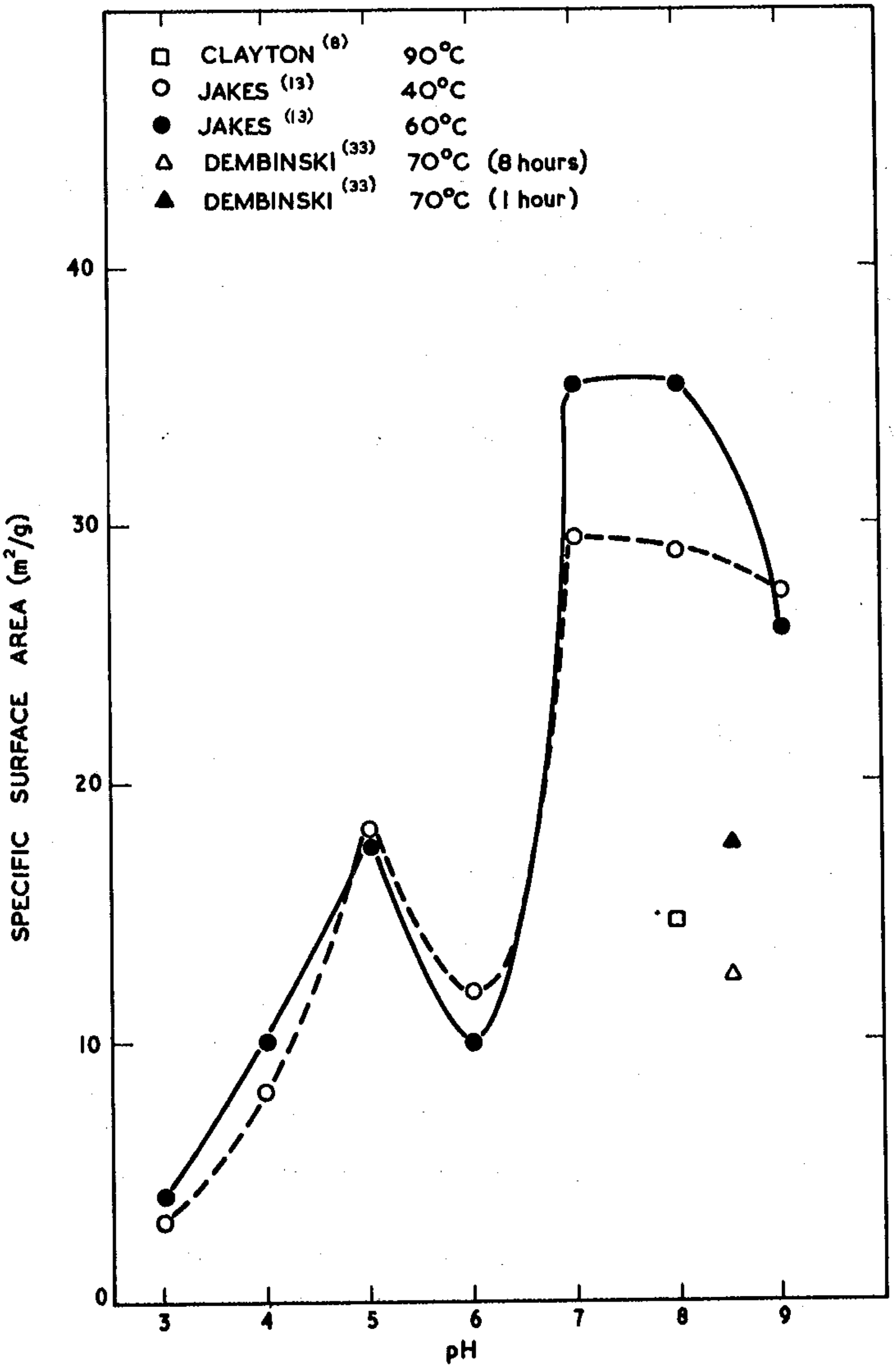

FIGURE 4. EFFECT OF FINAL pH OF PRECIPITATION ON THE SPECIFIC SURFACE AREA OF AMMONIUM URANATES

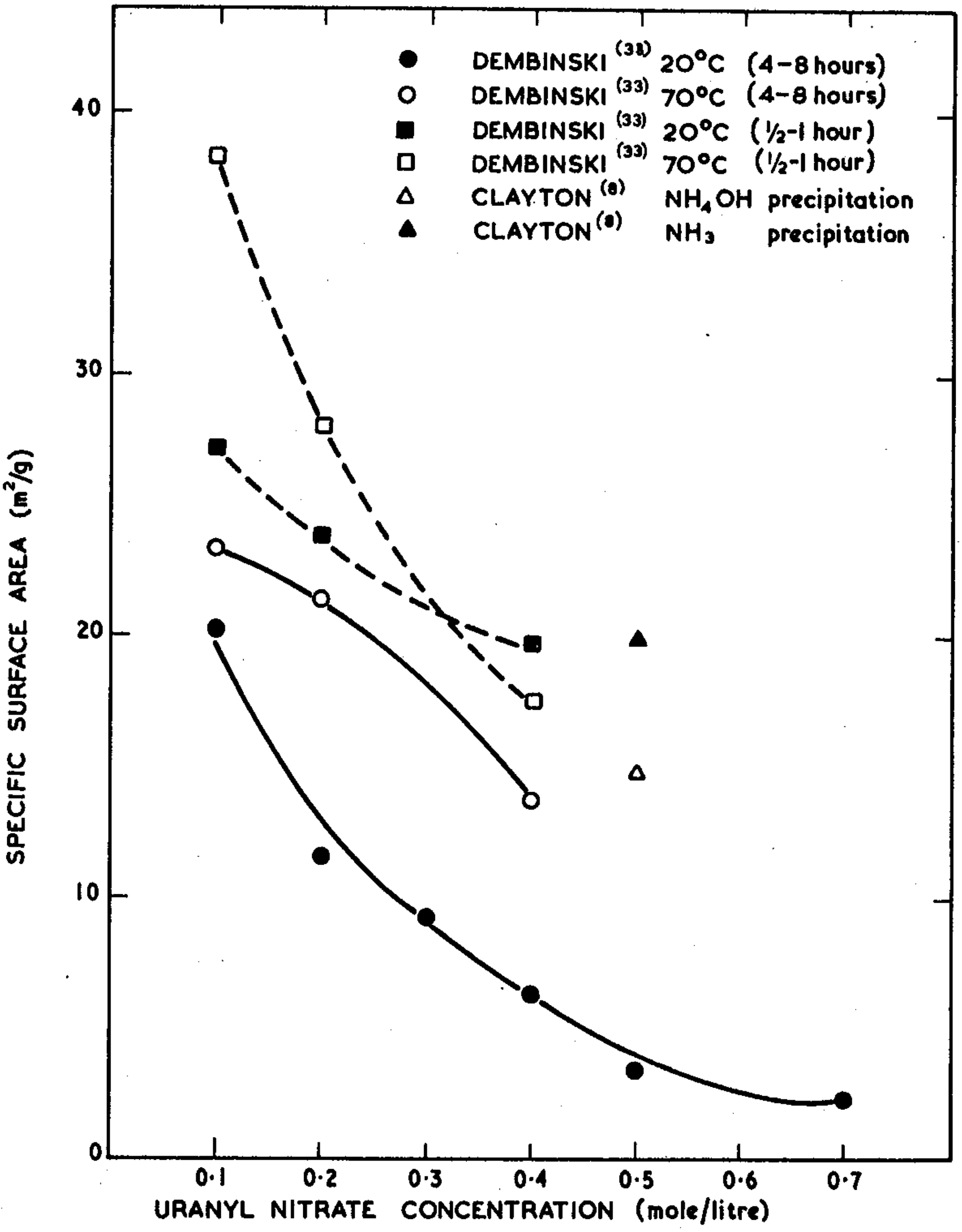

FIGURE 5. EFFECT OF URANYL NITRATE CONCENTRATION ON THE SPECIFIC SURFACE AREA OF AMMONIUM URANATES

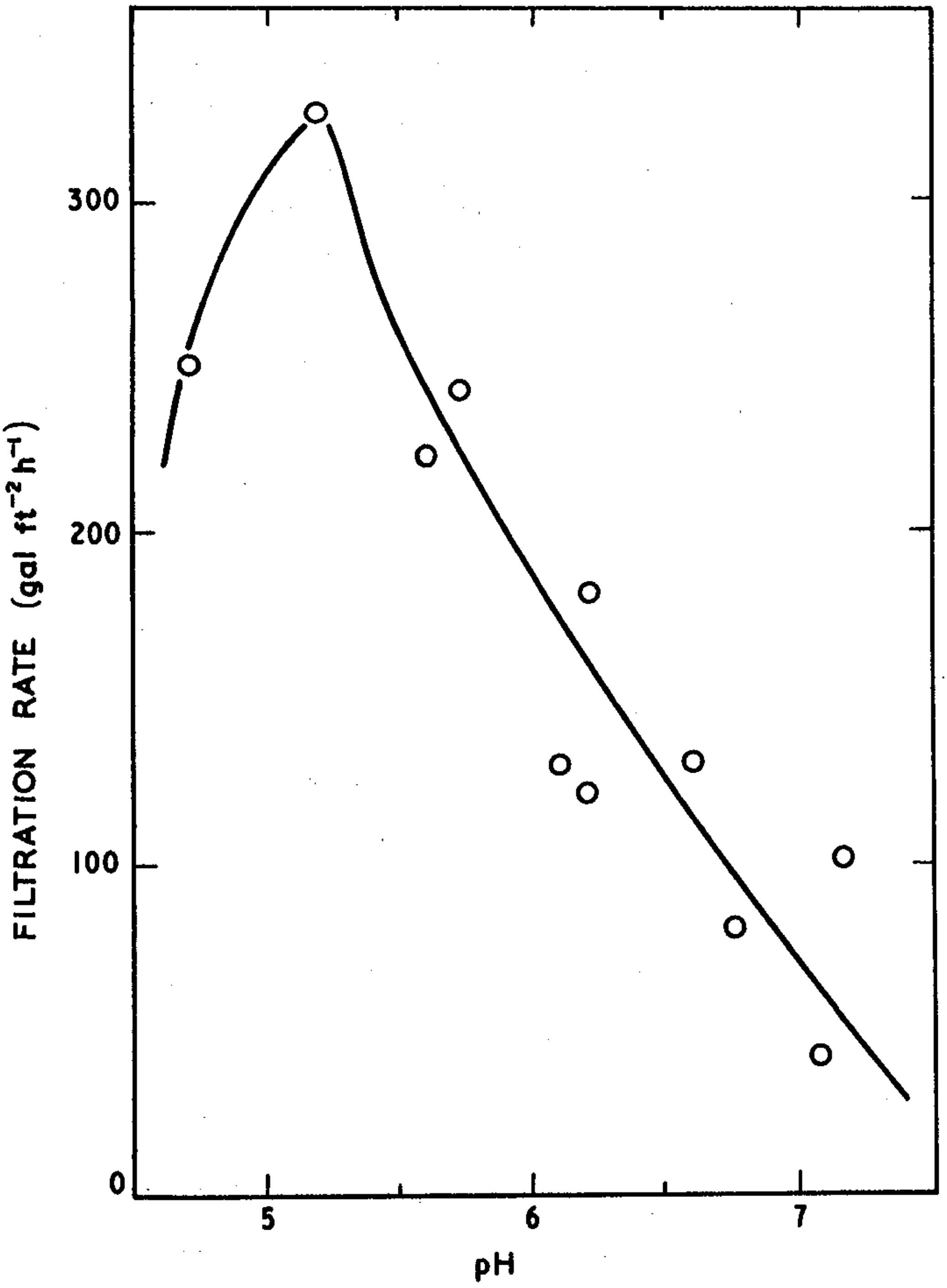

FIGURE 6. EFFECT OF FINAL pH OF PRECIPITATION ON THE RATE OF FILTRATION OF AMMONIUM URANATES - AFTER REINHART (37)

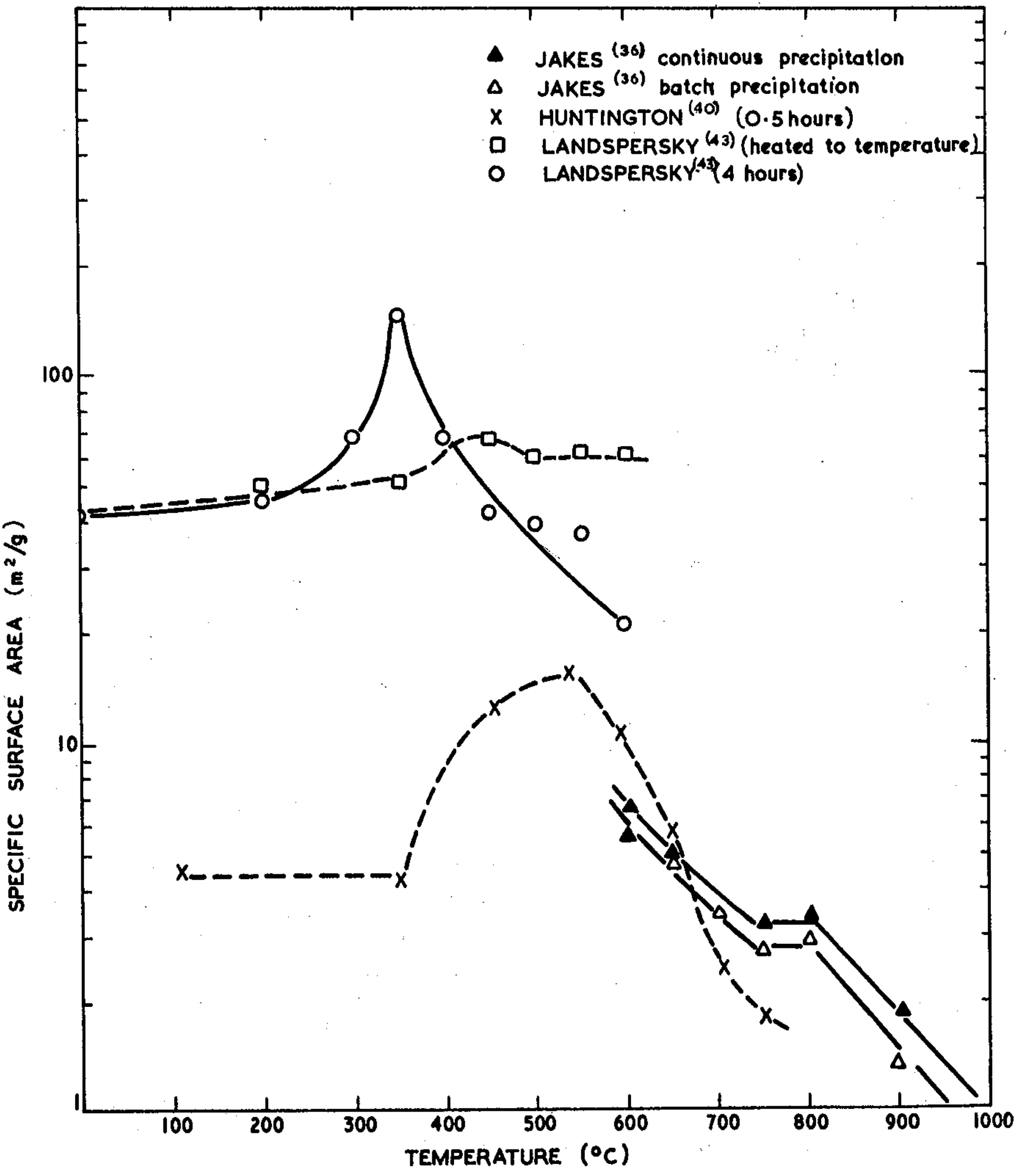

FIGURE 7. EFFECT OF CALCINATION TEMPERATURE UPON THE SPECIFIC SURFACE AREA OF POWDERS FORMED DURING THE DECOMPOSITION OF AMMONIUM URANATES

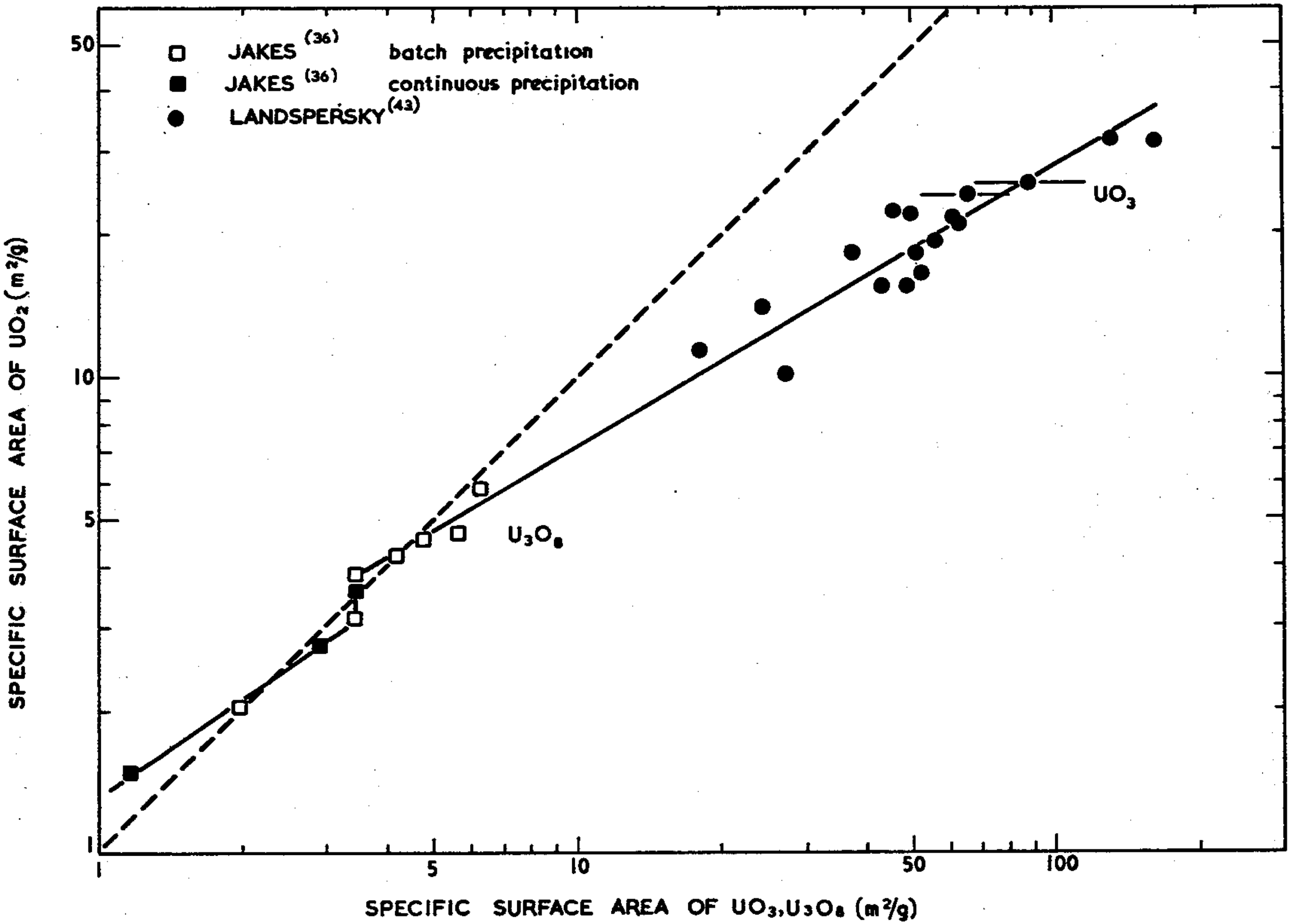

FIGURE 8. RELATIONSHIP BETWEEN THE SPECIFIC SURFACE AREAS OF PRECURSOR UO_3 / U_3O_8 AND THE UO_2 PRODUCED BY SUBSEQUENT H_2 REDUCTION