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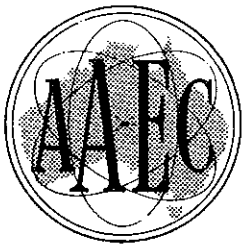

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THE INFLUENCE OF PRECIPITATION CONDITIONS ON THE PROPERTIES OF AMMONIUM DIURANATE AND URANIUM DIOXIDE POWDERS

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ABSTRACT

A comprehensive investigation of the factors affecting the properties of ADU precipitates in relation to the properties of the subsequent UO_2 powders in pellet fabrication is reported and the importance of precipitation parameters is demonstrated. Variables investigated include continuous single-versus two-stage precipitation, pH, residence time, washing of ADU to remove nitrate, and calcination-reduction conditions.

The most important variable was the pH at which precipitation occurred. In particular, this governed the size of agglomerates which determined the settling and filtering characteristics of the ADU slurry. In two-stage precipitation, the ADU properties were determined by the proportion of uranium precipitated at different pH values.

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ABSTRACT (continued)

Washing of nitrate from ADU appeared not to affect the properties of the subsequent UO_2 powder. Approximately 75 per cent of the initial nitrate was removed by washing once in demineralised water; more extensive washing caused only a slight further reduction in nitrate content and significantly reduced the filterability of the ADU slurry.

When ADU was reduced to UO_2 at 600°C in hydrogen, differences in the surface areas of the powders were markedly reduced but the agglomerate structure of the ADU was retained. ADU which was precipitated mainly at pH 3-4, and contained large agglomerates, gave UO_2 containing large agglomerates which sintered poorly and the pseudomorphs of the large agglomerates were still discernible in the sintered pellets. ADU precipitated at high pH contained small agglomerates and gave UO_2 powder which sintered readily to high density pellets with uniform microstructure. The settling rate of the ADU slurry gave an early indication of the likely sinterability of the resultant UO_2 powder since both were functions of agglomerate size.

Reasonably filterable ADU and sinterable UO_2 powders were prepared via single-stage precipitation at pH 7.2 or by two-stage precipitation in which less than 80 per cent of the uranium was precipitated in the first stage at pH 3.5 and the remainder in the pH range 7-8. Less stringent control was required in two-stage precipitation than in single-stage precipitation, but this was offset by the additional complexity of two precipitators and their auxiliaries.

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1. INTRODUCTION

Most types of commercial nuclear power reactors are fuelled with uranium dioxide in the form of sintered pellets with density close to theoretical. The uranium dioxide powder from which the pellets are fabricated is nearly always produced by the ammonium diuranate route. This involves precipitating an ammonium uranate, usually, though incorrectly, referred to as ammonium diuranate (ADU), from a purified source of uranium such as uranyl nitrate. The dry ADU is then converted to UO_2 powder in a reducing atmosphere.

The essential properties of UO_2 powder are chemical purity, so that neutron losses by absorption are low, and the ability to sinter reproducibly to a high density at relatively low temperatures. The microstructure of sintered UO_2 pellets must be reasonably homogeneous and free of gross defects and the UO_2 powder should therefore be homogeneous and free of tightly bound agglomerates.

There is considerable (often conflicting) evidence to show that the properties of the UO_2 powder produced from ADU depend on the conditions of ADU precipitation as well as the procedure used for converting the ADU to UO_2. This report describes a comprehensive investigation of the factors affecting the properties of ADU precipitates in relation to the properties of the subsequent UO_2 powders. These factors include single- versus two-stage precipitation, pH, residence time, washing of ADU precipitates to remove nitrate, and calcination-reduction conditions. The importance of agglomeration is emphasised because of its effect on the filterability of ADU and the sinterability of UO_2 powder. The advantages of two-stage versus single-stage precipitation are also discussed.

2. REVIEW OF PREVIOUS WORK

Many papers have been published concerning the preparation and properties of ADU and UO_2 powders and Woolfrey (1968) has reviewed this information emphasising the composition and morphology of these materials. In this Section, we consider briefly only the complex nature of ammonium uranates, the effect of precipitation conditions on some ADU properties, washing of ADU precipitates and the influence of precipitation conditions on UO_2 powder properties.

Various compositions have been reported for ammonium uranates, for example, Cordefunke (1962) found that four distinct compounds can be formed at different pH conditions with NH_3:U ratios 0.00, 0.33, 0.50 and 0.67. However Stuart and Whateley (1969) claimed that the ammonium uranate system is single phase and that the NH_3:U ratio can be varied continuously but Cordefunke (1970) disputed this. In this report compounds with different composition are not differentiated and all are referred to as ADU. It may be noted however that the diuranate, $(NH_4)_2 U_2O_7$, probably never exists in aqueous solution (Stuart and Whateley 1969).

The physical nature as well as the chemical composition of ADU changes with pH of precipitation. The size of ADU crystallites* decreases with increasing pH of precipitation (Stevenson 1964). Similarly the size of ADU agglomerates (Yatabe and Watson 1958) and the filterability of ADU slurries also decrease with increasing pH of precipitation. While the influence of ADU precipitation conditions on the properties of the subsequent UO_2 is important, examination of precipitation conditions in terms of the filterability of the ADU slurry is also of particular interest.

Reinhart et al. (1962) patented a method for producing readily filterable ADU continuously at a pH 5.0 to 6.5. However, this is a pH region very sensitive

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*The term crystallite refers to the ultimate particle in a powder. Where crystallites coalesce to form reasonably strong aggregates they are described as agglomerates.

to changes in feed rates and it is quite difficult to maintain a uniform product using this procedure. Stevenson (1964) suggested a more satisfactory approach for obtaining a readily filterable material on a continuous basis. The two reactant streams were contacted by countercurrent methods in a series of connected precipitators such that a sequential range of pH existed in the vessels. Most of the uranium was precipitated at pH 5.0 and below, where readily filterable ADU was produced. A precipitate with filtering characteristics equal to the best achieved with single-stage or batch precipitation was obtained while the control problems associated with Reinhart's method were eliminated. Smith et al. (1964) described the satisfactory utilisation of this principle in the U.K.A.E.A. fast reactor programme.

Vuillemey (1962) studied a two-stage ADU precipitation process in which ADU was formed at two separate levels of pH. This was similar to the multi-stage process described above in that a low pH was maintained in the first precipitator to produce a readily filterable material and then the pH was raised to above seven in the second precipitator to ensure that essentially all the uranium was recovered from the solution.

ADU precipitated from uranyl nitrate inevitably contains impurity nitrate ions most of which can be removed by washing the ADU with water (Cordefunke 1962). However the role of nitrate ions in the subsequent drying and calcination-reduction processes and their influence on the properties of the resultant UO_2 powder have not been reported. Unwashed ADU frequently contains visible amounts of ammonium nitrate crystals which are probably undesirable on safety grounds during drying and calcination-reduction. It is known that Eldorado Mining and Refining Ltd (Berry 1967), who produce UO_2, and U.K.A.E.A. Atomic Weapons Research Establishment (Smith et al. 1964) who produce UO_2 and mixed Pu - U oxides both wash their precipitates before further processing, but their reasons for doing so are not known.

The most important aspect of ADU precipitation is its effect on UO_2 powder properties, particularly sinterability. Doi and Ito (1964) found that the main features of ADU agglomeration, which were established in the precipitation, essentially persisted throughout calcination to UO_3 and subsequent reduction to UO_2 at temperatures below 600°C. Further high temperature firing of the loose UO_2 powder in hydrogen caused extensive grain growth due to sintering and this growth was found to be profoundly affected by the physical state of the precursor precipitate.

Kiessling and Runfors (1957) starting with ADU precipitated homogeneously from uranyl nitrate with urea, also found that the shape and size of the agglomerates were preserved through the chemical reactions involved in converting the ADU to UO_2. In addition, they found that the shape and size of the agglomerates influenced the sintering of cold-pressed pellets because sintering of crystallites within an agglomerate occurred much more readily than sintering between adjoining agglomerates. Several other investigators, including Yatabe and Watson (1958) and Carpenter et al. (1961), working on pilot plant development of UO_2 pellet manufacture, also noted a dependence of UO_2 sinterability on the method of ADU precipitation.

On the other hand, Ainscough and Oldfield (1962) and Fareeduddin et al. (1958) found little if any correlation between the precipitation conditions and the sintered densities of the resultant UO_2 pellets. However, Ainscough and Oldfield milled their UO_2 powders in a vibratory mill for two hours and this could have eliminated any differences in the virgin powders resulting from different precipitation conditions. Fareeduddin et al. found that the temperature of calcination of ADU had the greatest bearing of any production variable on the sinterability of UO_2. They also suggested that considerable changes in powder properties might have been introduced during granulation and pressing stages which, together with the effect of calcination temperature, could have largely eliminated the differences between precipitates.

It seems then, that the conditions of precipitation can have a major influence on the sintered density and microstructure of UO_2 pellets if subsequent processing does not alter the physical state of the powder. More vigorous processing tends to eliminate any differences between powders due to differences in precursor ADU precipitates.

The purpose of this work was to investigate comprehensively those precipitation parameters which caused changes in ADU slurry and powder properties and to determine those properties of ADU which influenced the properties of UO_2 powders in pellet fabrication. In particular we investigated in a coordinated manner the effect of pH in single- and two-stage precipitation on the filtering and settling characteristics of ADU slurries and on the sinterability of the subsequent UO_2 powders. Washing of ADU with demineralised water was studied to determine its effect on ADU and UO_2 properties. Reduction of ADU to UO_2 was examined to establish whether this step had a more important effect on the sinterability of the UO_2 powder than ADU precipitation conditions.

3. EXPERIMENTAL

3.1 Feed Materials

In the work reported here, most of the experiments used uranyl nitrate made by solvent extraction purification of Australian yellow cake in pilot plant equipment (Alfredson 1969). In some experiments uranyl nitrate produced by redissolving UO_2 or UO_3 powders was used. The latter material was checked for nuclear purity and adjusted to the same concentration and acidity as uranyl nitrate produced by solvent extraction.

The solvent extraction process produced uranyl nitrate with uranium concentration varying from 68 g/ℓ to 85 g/ℓ but it was adjusted to 70 ± 2 g/ℓ in all experiments. The acidity of the uranyl nitrate varied over only a small range from 0.05 N to 0.15 N.

Trace quantities of tributyl phosphate/kerosene solvent were carried over from the solvent extraction and could be detected in some batches as an organic film on top of the uranyl nitrate. This gave the uranyl nitrate a faint aromatic odour. Uranyl nitrate produced by dissolving UO_2 showed no signs of tributyl phosphate but the two uranyl nitrates gave identical results in precipitation.

The uranyl nitrate was always low in cation impurities. Typical impurity levels of material purified by solvent extraction are given in Table 1. In some instances the impurity level of certain elements, particularly iron, nickel, chromium, copper and zinc, in recycled uranium feed materials had increased as much as fourfold, but it is assumed that this did not affect precipitation since the impurity concentrations were still quite low.

Analytical grade ammonium hydroxide was used as the precipitant. In most cases it was diluted to approximately 11 N with demineralised water but in later experiments 28 weight per cent ammonium hydroxide (equivalent to 14 N) was used.

3.2 Precipitation Equipment and Method of Operation

The precipitators and other auxiliary equipment in the experimental rig are shown schematically in Figure 1. The two cylindrical precipitation vessels were 95 mm i.d. and the overflow pipes 0.36 m from the base. The measured operating volumes of the precipitators were 1970 ml for the first, and 1580 ml for the second precipitator which had a 6 mm thick 77 mm o.d. cylindrical baffle inside it. Both precipitators were jacketed by 152 mm o.d. Perspex tubes. This allowed the temperature of the precipitators to be controlled by passing heated water through the jackets. The contents of both precipitators were stirred by small

25 mm diameter paddles rotating at 2,000 rev/min. An excessively slow stirring speed (< 500 rev/min) did not give adequate mixing and a gelatinous precipitate resulted, while over a range of stirring speeds at about 2,000 rev/min the physical nature of the ADU precipitate appeared to be unaffected. In all the experiments described, the stirring speed was 2,000 ± 50 rev/min.

The liquid streams were delivered to the precipitators at controlled flow rates via constant volume displacement pumps. The flows remained constant within ± 1 per cent over long periods of operation. When operating as a two-stage precipitator, ammonium hydroxide was added to both the first and second reactors but uranyl nitrate was charged only to the first one. The ammonium hydroxide flow to the first reactor was adjusted to give a fixed amount of precipitation. The uranyl nitrate/ADU slurry then overflowed to the second reactor where further ammonium hydroxide was added to convert the remaining uranyl nitrate to ADU.

Two different techniques need to be used to control the operating conditions in the two reactors. The condition of the final slurry can be conveniently followed by pH measurement and an E.I.L. model 23A pH meter was used. A resistance thermometer was used in conjunction with the glass and reference electrodes to provide automatic temperature compensation ensuring a true e.m.f. output reading. The actual pH of the slurry changes with temperature, as the amount of ionisation in solution changes. For the system being studied, the pH decreased approximately 0.15 units per 10°C. It was therefore important to specify the temperature at which the pH was measured. However, in the operating region of the first reactor, pH measurement was insensitive to the extent of uranium precipitation and the actual percentage of uranium precipitated was determined to establish the operating point. This was done by withdrawing an aliquot of partially precipitated ADU/uranyl nitrate slurry from the first reactor, separating the ADU from the depleted uranyl nitrate by filtration and then determining the concentration of uranium in solution. A γ-absorptiometer (Yates and May 1970) was used to measure the uranium concentration so that the total operation could be completed in 10 minutes; the percentage precipitated was calculated from the decrease in uranium concentration. When the precipitation was carried out exclusively at one pH (that is, single-stage precipitation) the second precipitator was by-passed and the reaction was controlled by pH alone.

After precipitation, the ADU was washed three times by allowing the precipitate to settle, decanting the mother liquor, and then reslurrying in demineralised water. The washing reduced the amount of nitrate in the solids to a level below which it was difficult to remove any further nitrate (approximately 0.3 per cent). The washed ADU was filtered in a Buchner funnel and dried in an air oven at 50°C to constant weight.

3.3 Measurement of Properties of ADU Slurry

The two properties of ADU slurries of most interest are filterability and settling characteristics. Filtration is used for separating wet ADU from the mother liquor, and settling and decantation could be used advantageously as a prelude to filtration.

3.3.1 Settling

The hindered settling rate of the ADU slurry was generally measured at one concentration only, namely the concentration at which it was produced (90 - 100 g ADU/ℓ). In a few instances, the effect of concentration on the hindered settling rate of a particular slurry was determined and from this the free settling velocity was extrapolated to give a measure of agglomerate size. Two litres of ADU slurry was collected in a measuring cylinder and allowed to cool to room temperature. The slurry was then re-homogenised by shaking and stirring and then allowed to settle in the two-litre cylinder. At the concentrations studied, a

sharp interface was formed between partially settled ADU slurry and the clear supernatant liquid. The rate of subsidence of the interface was measured to give the rate of hindered settling.

3.3.2 Filterability

The filterability of the ADU slurry was characterised in terms of the specific filtration resistance (see Equation 2) which is independent of the slurry concentration and temperature, and determined only by the particle size and state of aggregation of the solids (Carman 1938).

Filtration involves the forcing of a liquid through a porous bed of solids by applying a pressure difference across the bed and can be treated quantitatively by application of the basic rate equation for fluid flow:

$$\text{Rate} = \text{Potential/Resistance} \quad . \qquad \ldots(1)$$

Development of this fundamental relationship in terms of measurable quantities leads to the equation (Perry et al. 1963):

$$\frac{t}{V} = \frac{\mu\, r_1\, c}{2PA^2} V + \frac{\mu R}{PA} \quad , \qquad \ldots(2)$$

where V is the volume of filtrate collected in time t, μ the viscosity of the filtrate, c the concentration of dry solids per unit volume of filtrate, P the pressure applied across the filter cake, A the area of the filter and R the resistance of the filter septum. Plotting $\frac{t}{V}$ versus V at constant pressure should give a straight line with a slope from which r_1, the specific filtration resistance can be determined, and with an intercept which gives the resistance of the filter septum.

For compressible filter cakes, r_1 is a function of P which can often be approximated by the equation:

$$r_1 = aP^s \quad , \qquad \ldots(3)$$

where a is a constant determined largely by the size of the particles forming the cake and s is the compressibility of the cake, varying from 0 for rigid incompressible cakes to 1.0 for very highly compressible cakes. For most industrial slurries, s lies between 0.1 and 0.8 (Perry et al. 1963).

Knowing the specific filtration resistance at constant pressure, the filtration rate can be calculated for given values of c and A. If a rotary drum vacuum filter is operated at constant pressure with fixed cake thickness and drum speed, the time taken to filter a given quantity of filtrate is proportion to $\sqrt{r_1}$ (Sowden and Stockdale 1961).

The apparatus used for determining the specific filtration resistance was a 100 mm diameter Buchner filter to which a known constant vacuum could be applied. The filtrate was collected in a graduated cylinder and the volume of filtrate collected as a function of time was noted. All determinations were made in duplicate or triplicate.

3.4 Measurement of ADU and UO_2 Surface Areas

The surface areas of both UO_2 and ADU powders were measured by the BET method (Brunauer et al. 1938) using nitrogen adsorption. Two different experimental rigs were used in this work. The results from both agreed within experimental error (± 10 per cent) using the procedures outlined below. The early surface area measurements were made on a classical BET rig where all adsorption measurements were taken at equilibrium conditions, using gas volume-pressure relationships.

The later ones were made using a continuous flow method developed by Nelsen and Eggertsen (1958) in which nitrogen is adsorbed by the sample at liquid nitrogen temperature from a gas stream of nitrogen and helium and eluted upon warming the sample. The nitrogen liberated is measured by thermal conductivity. The continuous flow method is faster and more samples can be prepared concurrently. The principles of gas adsorption are the same in this method as in the classical static method and the same assumptions about the area covered per nitrogen molecule need to be made, that is, that each adsorbed nitrogen molecule covers 16.2 $Å^2$.

Before nitrogen adsorption, the surface of the solid must be cleaned by heating it in a vacuum or in an inert atmosphere. When using the static gas adsorption rig a vacuum of 10^{-5} torr was used for cleaning the surface of ADU and UO_2. The ADU was cleaned at 50°C for 18 hr and the UO_2 at 300°C for 18 hr. Under these conditions, a vacuum of 10^{-5} torr could be obtained, indicating that no further gas was being released from the surface. When the continuous flow apparatus was used, the same conditions of temperature and time were used for sample preparation but instead of pumping to a vacuum, a stream of helium was passed over the samples to sweep away the adsorbed gases.

For ADU, the conditioning temperature is not critical and the measured value of surface area does not vary for conditioning temperatures over the range 50 - 200°C (Woolfrey, A.A.E.C. private communication). The UO_2 surface area depends on the conditioning temperature chosen. Below 300°C the surface of the UO_2 is not cleaned thoroughly, while above 300°C surface diffusion processes presumably begin to reduce the surface area.

3.5 Reduction of ADU to UO_2

All UO_2 powders were prepared in a batch-tray calcination-reduction reactor. The depth of powder in the trays was approximately 10 mm. A 30 per cent hydrogen/nitrogen mixture was generally used for reduction from ADU to UO_2 at temperatures from 400°C to 600°C over approximately two hours. After cooling to room temperature, the stoichiometric UO_2 powder was stabilised in a 2 per cent oxygen/nitrogen gas mixture for 16 hours before exposure to the atmosphere.

3.6 Determination of UO_2 Sinterability

The density of UO_2 pellets sintered in hydrogen at 1,500°C for four hours was taken as a measure of the sinterability of UO_2 powders. Before sintering, the UO_2 was ground to -100 mesh, formed into pellets and then isostatically pressed at 20 tons/in^2.

4. RESULTS AND DISCUSSION

4.1 General Observations on Precipitation

When ammonium hydroxide was slowly added to a fixed volume of uranyl nitrate at room temperature, the pH of the solution rose in the manner shown by the unbroken titration curve in Figure 2. Similar titration curves have been presented by Vuillemey (1962), Deptula (1962) and others. The first inflection point at pH 2 was due to neutralisation of free acid in the uranyl nitrate solution. Soon after the free acid was neutralised a yellow fluffy precipitate of low density was formed at about pH 3 but only at points of high ammonia concentration and it redissolved. The colour of the solution darkened as further ammonium hydroxide was added and finally a permanent precipitate was formed when approximately 0.9 equivalents of ammonium hydroxide had been added per mole of acid-free uranyl nitrate. As still more ammonium hydroxide was added the pH increased rather more slowly and, indeed, if addition of ammonium hydroxide was interrupted, the pH fell 0.5 pH unit in one hour. This indicates that the polymeric reactions involved in precipitate formation are slow to come to completion. Hence the titration curves shown in Figure 2 are not true equilibrium

curves but apply only at the specified rates of addition of ammonia. At a ratio of 1.9 equivalents of NH_4OH per mole of acid-free uranyl nitrate, there was a slight drop in pH when the titration was carried out at 23°C. The pH then rose more rapidly and precipitation was completed when approximately 2.4 - 2.6 equivalents of NH_4OH had been added per mole of acid-free uranyl nitrate (pH 6-7).

When the titration was done at above room temperature, the pH curve was displaced downwards on the ordinate scale, as shown in Figure 2, by the broken curve for precipitation at 52°C. This was due not only to a change of pH in the solution with temperature, but probably also to a more rapid rate of equilibration of the precipitation reactions.

Also included in Figure 2 is the relationship between percentage uranium precipitated and equivalents of NH_4OH added per mole of acid-free uranyl nitrate. This curve clearly shows that a final pH in excess of seven must be reached in order to recover essentially all the uranium from solution. The pH of the slurry did not alter greatly between the operating points where uranium began to be precipitated and where ninety five per cent of the uranium was precipitated. Thus, pH was not a sensitive parameter for the control of operating conditions in this region and the actual percentage of uranium precipitated was measured when precipitating in two stages.

4.2 Effect of Precipitation Conditions on ADU Crystallite Size

The effect of pH on ADU crystallite size may be demonstrated qualitatively by comparing transmission electron micrographs (Figures 3 and 4) of two ADU powders precipitated at widely separated ratios of ammonium hydroxide to uranyl nitrate. Both powders were washed in demineralised water and treated in an ultrasonic bath to disperse the agglomerates as far as possible.

Figure 3 shows an ADU precipitated at pH 3.5 with approximately 1.6 equivalents of ammonium hydroxide available for every mole of uranyl nitrate. A wide range of crystallite sizes is present in the field with the largest crystallite approximately 0.3 μm and the smallest 0.02 μm in width. Figure 4 shows an ADU precipitated with 2.6 equivalents of ammonium hydroxide per mole of uranyl nitrate (pH 7). There are no crystallites larger than 0.1 μm present in the field and the general impression is that the average crystallite size is smaller than in Figure 3.

Crystallites of different sizes are formed at different solution pH because the relative rates of nucleation of new crystallites and growth of existing crystallites depend on pH. As the solubility of the ADU decreases from approximately 16 g/ℓ at pH 3.5 (Figure 2) to 10^{-14} g/ℓ at pH 9 (Stevenson 1964) nucleation is increasingly favoured over crystal growth and a material with many small crystallites and high surface area is produced. At pH 3.5, however, the rate of nucleation is slower because of the lower supersaturation ratio, and larger crystals tend to be produced because crystal growth is favoured.

Surface area measurements also reveal this same dependence of ADU crystallite size on pH of precipitation. The surface mean diameter of crystallites may be estimated using the equation:

$$\bar{d} = \frac{6}{\rho S} \text{ microns} \quad ,$$

where $\bar{d}$ is the surface mean diameter of crystallites in μm,

defined as $\frac{\Sigma n_i d_i^3}{\Sigma n_i d_i^2}$,

n_i is the number of particles of diameter d_i

ρ is real density in g cm^{-3}, and

S is specific surface area in m^2 g^{-1}.

If the surface roughness or the internal porosity of the ADU crystallites does not change with size, then their measured surface area is inversely proportional to the surface mean crystallite diameter.

The surface areas of the two ADU powders shown in Figure 3 and Figure 4 were respectively 4.8 m^2 g^{-1} and 14.1 m^2 g^{-1}. If the average density of ADU is taken as 4.97 g cm^{-3} (computed from the X-ray structures for ADU postulated by Debets and Loopstra (1963)), then the ADU powders above should have consisted of crystallites of respective surface mean diameter 0.25 μm and 0.09 μm. In fact, the largest crystallites in Figures 3 and 4 had widths of 0.3 μm and 0.1 μm respectively, but the average widths were significantly smaller. Hence the surface area of these powders should have been somewhat larger than indicated above if all the surfaces of the crystallites were available for the adsorption of nitrogen in measuring the surface area. Even in Figures 3 and 4 where the powders have been dispersed in an ultrasonic bath, it can be seen that the crystallites overlap and adhere quite extensively. Some adjoining surfaces are apparently not available for nitrogen adsorption, and for this reason, and possibly others discussed in Section 4.5.3, there is no exact relationship between the measured nitrogen surface area and the observed crystallite size of the ADU.

Figure 5 shows the range of ADU surface areas which were produced at different pH values by precipitation in a single stage. The surface area of ADU precipitated at pH 8.4 was seven times larger than that of material precipitated at pH 3.5. Conversely the average crystallite size of ADU precipitated at pH 3.5 would be expected to be approximately seven times as great as that of ADU precipitated at pH 8.4.

In two-stage precipitation the available uranium is precipitated at two distinct pH levels. The fraction precipitated in the second stage can either form new crystallites or increase, by crystal growth, the size of crystallites previous nucleated in the first stage. Transmission electron micrographs of ADU products precipitated in two stages show a wide range of crystallite sizes but determination of an exact distribution is difficult and was not attempted. Surface areas of ADU powders precipitated in two stages with various combinations of ammonium hydroxide availability are shown in Table 2. As the percentage of uranium precipitated in the second stage at pH 7.6 to 7.8 increased, the surface area of the product increased indicating that most of the uranium precipitated in the second stage formed new crystallites, smaller than those precipitated in stage one. If appreciable crystal growth had occurred in the second stage (rather than nucleation) then the surface area of the ADU would not have increased much above 5 m^2 g^{-1}.

Two-stage precipitation can be used for producing an ADU powder of low surface area (< 8 m^2 g^{-1}) with complete recovery of uranium. In single-stage precipitation, ADU with low surface area can only be produced if less than 100 per cent of the uranium is precipitated at pH less than 6.

4.3 Filterability and Settling Characteristics of ADU Slurries

These two properties of ADU slurries are a measure of the rate of liquid passing through a fixed arrangement of solids. Their dependence on the conditions of precipitation are similar and are described together.

Figure 6 shows typical experimental data for filtrate volume (V) against time (t) measured at a pressure drop of 300 torr across the filter cake and these data are shown in Figure 7 as filtrate volume against $\frac{t}{V}$ in accordance with Equation 2. For slurries of equal solids concentration, the slopes of the lines in Figure 7 are proportional to the specific filtration resistances which are discussed in the following Sections.

ADU slurries are compressible and the specific filtration resistance varies with the pressure applied across the filter cake. Figure 8 shows the effect of pressure on the specific filtration resistance of an ADU precipitated in one stage at pH 7.2. The slope of the line is 0.26 indicating that the filter cake is quite compressible. A constant pressure drop of 300 torr across the filter cake was adopted for general use in this work and applies to the remainder of the data in this report.

Figure 9 shows some typical data for settling of the same ADU slurries as in Figures 6 and 7. Hindered settling rates were calculated from the straight line portion and are discussed in the following Sections of this report. The second region, where the rate of subsidence is much slower, corresponds to bed compaction. It is also interesting to note that the final bed volume is an inverse function of the rate of hindered settling. While these factors may be of interest in thickening of ADU slurries, they were not investigated further in this work.

4.3.1 Effect of pH on the filterability of single-stage ADU

Table 3 compares the settling characteristics and filterability of ADU slurries precipitated in one stage at various values of pH. The ADU produced at pH 3.5 settled very rapidly and filtered fast but as the pH of precipitation increased above pH 6.6, the settling rate fell off and predictably the slurry became more difficult to filter. The specific filtration resistance of ADU precipitated at pH 8.4 was 49 times that of ADU precipitated at pH 3.5. Thus it would take seven times as long to filter the former slurry as the latter.

In the pH region 6.6 to 7.2, measured at 50°C, the properties changed particularly rapidly. This region coincides with the inflection point in the titration curve (Figure 1) and small changes in the flow rate of either reactant cause appreciable changes in the pH of the solution as well as associated large changes in the slurry properties. In Table 3, data for two slurries produced under nominally identical conditions of pH 7.2 show that initial settling rates and specific filtration resistances varied by more than a factor of two. This indicates the sensitivity of ADU properties to pH in this region and the need for close control.

4.3.2 Filterability of ADU precipitated in two stages

In the same way that the surface area of ADU precipitated in two stages can be varied over a wide range by altering the proportion of total uranium precipitated in each of the stages, so the filterability and settling characteristics can be modified by precipitating different amounts of uranium at pH 3.5 and at some higher pH above 7. Table 4 shows this variation for a series of ADU materials with different percentages of uranium precipitated in stage one.

When less than approximately 83 per cent of the uranium was precipitated in the first stage at pH 3.5, the slurry properties were similar to those of ADU precipitated in one stage at pH 7.2 and above. The ADU slurry in which only 55 per cent of the uranium was precipitated in stage one was almost as difficult to filter as the single-stage ADU listed in Table 3 precipitated at pH 8.4. However, when more than 90 per cent of the uranium was precipitated in stage one, the ADU was as filterable as material precipitated exclusively at pH 3.5. The important advantage of two-stage precipitation is that it enables recovery of all the uranium from solution as well as producing a very filterable product.

Precipitation at pH 3.5 will not achieve the complete recovery of uranium although it gives a very filterable product.

Further, the exact pH in the second stage was unimportant in determining the filterability of the ADU if the great majority of the uranium had already been precipitated in the first stage at pH 3.5 (Table 5). Although there was a slight decrease in filterability with increasing final pH, only fairly coarse control of pH in the second stage of a two-stage precipitator had to be maintained to ensure a fairly uniform product.

The filterability of ADU precipitated in two stages increased with total residence time, that is, the total time of residence of the slurry in both reactors (Table 6). The improved filterability is mainly attributed to the longer residence at pH 3.5 where, because of the solubility of ADU, large crystallites can grow at the expense of small ones which redissolve. At pH 7 and above, a longer residence time would have no effect on the crystallite size distribution of ADU because the solubility of ADU is very small in this region.

An increased temperature should also favour crystal growth at pH 3.5 by increasing the solubility of ADU. The solubility at pH 7 and above is so low that temperature would not be expected to cause a marked change in crystallite size distribution. However, the effect of temperature on precipitation was not investigated in this work.

4.4 Agglomeration in ADU

The effect of pH on ADU agglomerate size may be demonstrated by comparing Figures 10 and 11 which show two ADU powders precipitated at pH 7.2 and pH 3.5 respectively. The ADU precipitated at pH 3.5 contained numerous large agglomerates of size 20 - 24 μm while ADU precipitated at pH 7.2 contained agglomerates of approximately 3 μm which were further connected together into chains and secondary clusters. Isolated agglomerates of 3 μm size would not settle at the rates measured, (0.07 - 0.18 mm/sec, Table 3) and therefore in the slurry precipitated at pH 7.2 the hindered settling rate must be determined by some larger network of agglomerates around which the fluid moves. This larger cluster of agglomerates was probably held together quite weakly but the 3 μm agglomerates were strong and their pseudomorphs could be found in later stages of UO_2 pellet manufacture.

The hindered settling rate is a function of agglomerate size and slurry concentration (Steinour 1944). Figure 12 gives data for hindered settling rate as a function of slurry concentration for the two ADU materials mentioned above. By extrapolating to zero concentration, an estimate of the size of agglomerates can be obtained using Stoke's law for free settling spherical particles. Assuming the density of the agglomerates is say half the density of the ADU crystallites density, the corresponding sizes of the agglomerates in the slurries in Figure 12 are 41 μm and 29 μm. The 41 μm estimate agrees reasonably with the size of the agglomerates seen in Figure 11 but the 29 μm agglomerates for the pH 7.2 slurry must be larger networks of the 3 μm agglomerates seen in Figure 10.

Fast settling and readily filterable slurries, produced predominantly at pH 3.5 contained both large crystallites and large agglomerates. ADU precipitates produced exclusively at high pH contained smaller crystallites as well as smaller agglomerates. The different rates of settling were determined by the size of agglomerates while filterability was probably affected by both crystallite size and agglomerate size. This is discussed further in Section 4.5.2.

4.5 Effects of Washing ADU

4.5.1 Effect of washing on the chemical composition of ADU

As well as reducing the amount of nitrate in ADU, washing with demineralised water also removed NH_3 or NH_4^+. Part of the ammonia was removed as NH_4^+ associated with nitrate in ammonium nitrate but some was replaced in the ADU structure (Cordefunke 1962 and Stuart and Whateley 1969). Figure 13 shows the progressive reduction of nitrate and ammonia in an ADU that was repeatedly washed by allowing the ADU slurry to settle, decanting the clear liquid overburden and then reslurrying it again in demineralised water. With each washing step, the ADU was allowed to settle to approximately twenty per cent of the original slurry volume before decantation. Finally the slurry was filtered and dried at 50°C after the indicated number of washing steps.

The first wash removed approximately 75 per cent of the nitrate present in the as-precipitated ADU but subsequent washing reduced the nitrate level only slightly. A small amount of nitrate seemed to be quite tightly held in the ADU and could not be removed by this kind of washing. Approximately 15 per cent of the ammonia in the ADU was also removed by the first wash and further ammonia was removed with subsequent washing operations. Cordefunke (1962) reported a similar gradual reduction in ammonia content of ammonium uranates exposed to moist air. His system, however, was free of nitrate.

4.5.2 Effect of washing on the settling rate and filterability of ADU slurries

When ADU slurries which settled rapidly were vigorously washed several times in the manner previously described it was found that the slurry did not settle completely to leave a clear liquid overburden. Instead, the liquid above the settled bed of ADU was cloudy and contained fine ADU particles which were too small to settle at a measurable rate. These fine particles of ADU apparently became peptised as the ionic composition of the liquid and the ADU surfaces were changed by the washing. However, the bulk of the solids still settled at the same rate as before, indicating that the agglomerate size was not appreciably changed by the small amount of peptisation.

The partial peptisation, however, had a large effect on the filterability of the ADU slurry (Table 7). The ADU in Table 7 was precipitated in two stages with 85 per cent of the uranium precipitated in the first stage. Filterability was essentially unchanged after the first two washing steps but after the third it deteriorated. The deterioration coincided with the onset of peptisation which occurred as the nitrate was washed from the ADU. The fine detached ADU particles apparently lodged in the voids between packed agglomerates in the filter cake, making it less permeable to the fluid being filtered. If the ADU crystallite size alone determined the filterability of the ADU then no deterioration of filtering properties with peptisation would have occurred and it appears that the size of the ADU agglomerates determined its filterability as well as its settling rate.

Thus repeated washing of highly agglomerated, filterable ADU materials should be avoided since it substantially reduces the filterability of the ADU without further reducing the nitrate content. Less filterable ADU, precipitated at high pH was not noticeably affected by repeated washing.

4.5.3 Effect of washing on ADU and UO_2 surface areas

In unwashed ADU, significant amounts of ammonium nitrate may have prevented the nitrogen gas, used for measuring the surface area, from reaching all the ADU surfaces. Washing removed some of the ammonium nitrate and the

measured ADU surface area increased as more of the ADU surfaces became accessible to the nitrogen gas (Table 7). Most of the surface area change occurred during the first wash when 75 per cent of the ammonium nitrate was removed. After the first wash the measured ADU surface area remained essentially constant.

The nitrate content of ADU did not affect the surface area of UO_2 powder produced from it. Table 8 shows results for two ADU powders which were precipitated and reduced under identical conditions. The first, however, was spray dried (Hirst - A.A.E.C. Unpublished Work) without any prior washing and this resulted in a very high ammonium nitrate content (8.9 per cent NO_3^-). As expected, the measured ADU surface areas were quite different but when the two ADU powders were both reduced at 600°C the surface areas of the resulting UO_2 powders were essentially identical.

Thus small changes in nitrate content produced by washing ADU with demineralised water before conventional filtering and drying are even less likely to affect UO_2 surface area and there appears to be little incentive for washing ADU except possibly the removal of visible amounts of ammonium nitrate.

4.6 Influence of ADU Precursor on UO_2 Properties

Figure 14 shows the surface area of UO_2 powders produced from a range of ADU powders by reduction at 600°C. The surface area was only slightly dependent on the surface area of the parent ADU and much larger changes in UO_2 surface area can be produced by changing the reduction temperature (Janov and Alfredson - unpublished work). Thus the conditions of ADU precipitation are not a major factor in determining the surface area of the subsequent UO_2 powder. This property is more readily controlled by the reduction conditions.

The size of UO_2 agglomerates, however, was determined by the manner in which the parent ADU was precipitated. Reduction at about 600°C chemically converted the ADU to UO_2 and caused changes in the size of crystallites but the agglomerates remained essentially intact. This dependence of UO_2 agglomerate size on the ADU can be seen by comparing Figures 11 and 15. The former shows a two-stage ADU which was produced by precipitating 95 per cent of the ADU in stage one at pH 3.5. This was a fast settling, readily filterable ADU and contained many agglomerates of 20 - 24 μm in diameter. Figure 15 is a scanning electron micrograph of UO_2 powder produced from this ADU by reduction at 600°C. The field contains a number of agglomerates larger than 20 μm in diameter and generally the powder is aggregated into discrete spherical agglomerates of mean size approximately 10 μm. With the increase in crystallite density from 4.97 g/cm^3 for ADU to 10.96 g/cm^3 for UO_2, some reduction in agglomerate size, of the order of 30 per cent, may be expected. Thus the size of the UO_2 agglomerates is governed primarily by precipitation conditions which can induce tenfold differences.

In the case of single-stage ADU precipitated at pH 7.2, the agglomerates were up to 2 - 3 μm in diameter but less distinct because they tended to cluster and form loosely bound groupings (Figure 10). UO_2 produced from this material by reduction at 600°C is shown in Figure 16. The largest dense continuous area of material in the field is approximately four microns across, located in the upper left hand corner of the micrograph. Agglomerates are not as discernible in this type of UO_2 but clearly no large agglomerates of the type shown in Figure 15 are present. The small UO_2 agglomerates are approximately the same size as the ADU agglomerates established in precipitation at pH 7.2.

Thus the conversion of ADU to UO_2 by calcination and reduction at 600°C substantially reduced differences in the surface areas of the powders but the agglomerate structure established during precipitation was essentially retained. The surface area of UO_2 powder is largely independent of the parent ADU and is governed by the reduction temperature.

4.7 Influence of ADU on the Sinterability of UO_2

It is generally recognised that UO_2 powders with large surface areas are more sinterable than those with low surface areas. This applies only to UO_2 powder prepared from the same ADU. In this work, the size of the agglomerates in the powder was found to be a more important parameter than surface area. Table 9 lists the sintered densities attained at 1,500°C for a series of powders with widely different preparation histories. The surface areas of the UO_2 powders ranged from 15.1 m^2/g to 2.8 m^2/g and the size of agglomerates ranged from 2 - 3 μm agglomerates for powders 2, 8 and 13 to agglomerates of greater than 20 μm for powders prepared from ADU precipitated predominantly (say > 90 per cent uranium) at pH 3.5. There is no general correlation between the UO_2 surface area and the sintered density of the UO_2 pellets. The sintered density of powders with a surface area 4 - 5 m^2/g ranged from 10.60 g/cm^3 to 9.15 g/cm^3. Dembinski et al. (1966) also failed to find any correlation between the surface area and sinterability of UO_2 powders prepared from different ADU powders.

The effect of percentage uranium precipitated at pH 3.5 on the sintered density achieved with UO_2 powder derived from these ADU materials is shown in Figure 17. The greater the amount of uranium precipitated at pH 3.5 the greater was the proportion of large agglomerates in the ADU and the ensuing UO_2 powder. As the percentage uranium precipitated at pH 3.5 increased above 75 per cent, the sintered density achieved with UO_2 powders derived from the ADU decreased rapidly. This break in the curve coincides with a marked change in ADU slurry settling characteristics at about 80 per cent uranium precipitated at pH 3.5 (Table 4).

Both the ADU settling characteristics and the sintered density of the UO_2 pellets depend on the size of agglomerates existing in the respective powders. Thus the settling rate of an ADU slurry is an early indication of the sinterability of the subsequent UO_2. Yatabe and Watson (1958) found the same correlation between sinterability of UO_2 and the settling rate of the parent ADU slurry for single-stage precipitation.

The large agglomerates present in poorly sinterable UO_2 powder affected the microstructure of the sintered pellets (Figure 18). Numerous isolated dense areas greater than 10 microns in diameter are visible in the etched polished section of the pellet and these were probably produced by sintering within large single UO_2 agglomerates. After the initial sintering within agglomerates, the contact between adjacent agglomerates is apparently not intimate enough to facilitate further sintering to high overall pellet densities and extensive intergranular porosity remains. Pellets fabricated from UO_2 containing only small agglomerates have much smaller grains and generally a denser pellet with uniform microstructure is obtained (Figure 19).

When the large UO_2 agglomerates present in material produced from filterable ADU were micronised before pressing and sintering, the density of the sintered pellets was appreciably increased. Grinding and high pellet pressing pressures were used by the Mallinckrodt Chemical Works to manufacture dense pellets from coarse non-sinterable UO_2 powder produced via thermal denitration (Harrington 1957). In the present work, the sintered densities of pellets produced from powder number 4 (Table 9) were upgraded by grinding the UO_2 powder in a Turbula mixer with steel balls for periods up to 21 hours (Table 10). Unfortunately the grinding also increased the concentration of iron impurities in the powder and this also may have enhanced sintering.

5. SUMMARY

This investigation of ADU precipitation, washing and calcination-reduction conditions has demonstrated the importance of precipitation parameters in determining the properties of ADU slurry and powder and the properties of the subsequent UO_2 powder in pellet fabrication.

The most important process variable studied in this work was the pH at which uranium was precipitated. It determined the size of ADU crystallites but more importantly it also determined the size of ADU agglomerates. The ADU slurry settling characteristics and filterability were a function of agglomerate size and the agglomeration which was established during precipitation persisted throughout subsequent process operations and was still evident in sintered pellets.

ADU precipitated at pH 3-4 contained large agglomerates which settled rapidly and were easy to filter. On the other hand, ADU precipitated at higher pH contained smaller agglomerates, settled more slowly and was more difficult to filter. When uranium was precipitated in two stages at different pH, the properties of the final product were determined by the proportion of uranium precipitated in each pH region. If more than 90 per cent of the uranium was precipitated at pH 3.5 in the first stage and the pH was then raised to above 7, the final product was very similar to material precipitated exclusively at pH 3.5. Further, the filterability of this type of ADU precipitate was not very sensitive to pH in the second stage but increased with an increase in total residence time. The important advantage of two-stage precipitation is that it enables complete recovery of uranium while producing a highly filterable ADU product. Precipitation at pH 3.5 in a single stage also produces a filterable material but not all the uranium is recovered.

These findings on the dependence of settling rate and filterability of ADU on the conditions of precipitation are in general agreement with other workers, particularly the work of Vuillemey (1962) on two-stage precipitation. Whereas Vuillemey defined operating conditions in terms of amounts of reactants present in each stage of precipitation, in this work the actual percentage of uranium precipitated in each stage was measured directly, leading to a better understanding of the precipitation process.

Within the scope of this work, no justification was found for washing ADU with water before further processing, except possibly to remove visible quantities of ammonium nitrate which may be undesirable on safety grounds during drying and calcination-reduction. Approximately 75 per cent of the nitrate impurities were readily washed out of ADU but although their removal increased the measured ADU surface area, the UO_2 surface area was unaltered. More extensive washing did not reduce the nitrate content appreciably but in some instances substantially decreased the filterability of ADU.

When ADU was reduced to UO_2 at 600°C, differences in crystallite size (surface area) were almost eliminated but differences in ADU agglomerate size were retained in the UO_2 powder.

The sintered density achieved in UO_2 pellets was related to the size of agglomerates in the UO_2 powder. ADU containing large agglomerates gave UO_2 with large agglomerates which did not sinter to a high density and the pseudomorphs were still discernible in the sintered pellets with large intergranular pores between them. The density of pellets produced from this type of powder was substantially increased when the powder was ground to break up the large agglomerates before sintering. ADU containing small agglomerates gave UO_2 powder which sintered, without the need for grinding of the powder, to high density pellets with uniform microstructure. As the precipitation conditions (particularly pH) determine the agglomerate size of both ADU and UO_2 powder, careful control of the precipitation is essential if UO_2 pellets with consistently high density are to be produced. The settling rate of ADU slurry was an important early indication of the sintered density likely to be achieved with the subsequent UO_2 powder in pellet manufacture.

Single-stage precipitation at pH 7.2 (measured at 50°C) gave essentially complete precipitation of uranium, and a reasonably filterable ADU, and the subsequent UO_2 powder sintered at 1500°C to 10.5 - 10.6 g/cm^3. Similar material was prepared by two-stage precipitation when less than 80 per cent of the uranium was precipitated in the first stage at approximately pH 3.5 and the remainder

precipitated in the second stage in the pH range 7 to 8. Two-stage precipitation was used to give very filterable ADU materials but the resultant UO_2 powders would have to be micronised before sintering if high pellet densities are required.

Close control was required for single-stage precipitation at pH 7.2 because small changes in the flow rates of reactants caused appreciable changes in pH and consequent changes in agglomerate size and filterability of the ADU and sinterability of the subsequent UO_2 powder. Less stringent control was required in two-stage precipitation but this was off-set by the additional complexity of two precipitators and associated auxiliaries.

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TABLE 1

TYPICAL SPECTROGRAPHIC ANALYSIS OF IMPURITIES

IN PURIFIED URANYL NITRATE

Element	ppm, U basis
Al	< 10
B	< 1
Cd	< 1
Cr	< 10
Co	< 1
Cu	10
Fe	24
Pb	1
Mg	< 10
Mn	< 1
Mo	< 1
Ni	< 2
Si	5
Na	40
V	< 1
Zn	< 15

TABLE 2

EFFECT OF PRECIPITATION CONDITIONS ON ADU SURFACE AREA

Temperature of precipitation	53°C
Total residence time	34 min.
Speed of stirrers	2000 rev/min.
pH in Stage Two	7.6 - 7.8

Percentage Uranium Precipitated in Stage One	Equivalents NH_4OH per Mole Uranium in Stage One	pH in Stage One	Percentage Uranium Precipitated in Stage Two	Measured Surface Area of ADU Product m^2/g
45	1.47	3.3	55	25.6
62	1.65	3.4	38	16.8
68	1.79	3.4	32	15.5
73	1.86	3.4	27	14.0
85	2.14	3.5	15	8.0
88	2.21	3.6	12	7.0
100	2.30	3.6	-	5.0

TABLE 3

EFFECT OF pH ON THE FILTERABILITY OF ADU PRECIPITATED IN ONE STAGE

Temperature of precipitation	50°C
Residence time	8 min.
Stirrer speed	2000 rev/min.

pH of Precipitation (measured at 50°C)	Specific Filtration Resistance m/g	Initial Settling Rate of ADU slurry mm/sec
8.4	7.84×10^8	0.02
7.2	1.93×10^8	0.07
7.2	0.52×10^8	0.18
7.1	1.00×10^8	0.19
6.6	0.13×10^8	0.90
3.5	0.16×10^8	rapid (> 0.90) but no clear interface

TABLE 4

EFFECT OF PERCENTAGE OF URANIUM PRECIPITATED IN STAGE ONE ON THE FILTERABILITY OF TWO-STAGE ADU

Total residence time	34 min.
pH in Stage Two	8.0 ± 0.1
Temperature of precipitation	50°C

Percentage Uranium Precipitated in Stage One	Specific Filtration Resistance m/g	Initial Settling Rate mm/sec
55	4.5×10^8	0.07
80	1.9×10^8	0.15
83	1.05×10^8	0.18
90	0.24×10^8	0.83
95	0.10×10^8	1.37

TABLE 5

EFFECT OF pH IN STAGE TWO ON FILTERABILITY OF TWO-STAGE ADU

Total residence time	34 min.
Stirrer speed	2000 rev/min.
Per cent uranium precipitated in Stage One	88-90
Temperature of precipitation	50°C

pH in Stage Two	Specific Filtration Resistance m/g	Initial Settling Rate mm/sec
7.3	0.24×10^8	0.67
7.9	0.24×10^8	0.83
8.2	0.63×10^8	0.83
9.1	0.94×10^8	0.33

TABLE 6

EFFECT OF RESIDENCE TIME ON FILTERABILITY OF TWO-STAGE ADU

Percentage uranium precipitated at pH 3.5	82%
pH in Stage Two	8.2
Temperature of precipitation	50°C
Stirrer speed	2000 rev/min.

Residence Time min	Specific Filtration Resistance m/g	Initial Settling Rate mm/sec
16	2.36×10^8	0.15
64	0.26×10^8	1.02

TABLE 7

EFFECT OF WASHING ON FILTERABILITY AND SURFACE AREA OF ADU

Treatment	Specific Filtration Resistance, m/g	NO_3^- (%)	Surface Area m^2/g
Unwashed	1.07×10^8	2.13	5.3
Washed once	0.83×10^8	0.56	8.2
Washed twice	0.74×10^8	0.36	8.2
Washed three times	2.52×10^8	0.26	8.5

TABLE 8

EFFECT OF NITRATE ON REDUCTION OF ADU TO UO_2

ADU Preparation	% NH_3	% NO_3^-	ADU Surface Area m^2/g	UO_2 Surface Area m^2/g
Spray-dried	3.17	8.9	2.8	5.1
Washed, filtered, tray dried	2.78	0.65	14.3	5.0

TABLE 9

SINTERED DENSITIES OF UO_2 PELLETS PREPARED FROM A VARIETY OF ADU POWDERS

Sintering conditions	4 hr, at 1500°C
Pressing pressure	20 tons/in^2
Powder size before pressing	-100 mesh

Powder No.	Type of Precipitation	Per Cent Uranium Precipitated at pH 3.5	pH in Single-state Precipitation	Actual Temperature of Reduction °C	UO_2 Surface Area m^2/g	UO_2 Sintered Density g/cm^3
1	Two-stage	95		700	2.8	9.00
2	Single-stage		7.2	700	2.9	10.51
3	Two-stage	80		700	3.0	9.80
4	Two-stage	95		620	3.4	9.45
5	Single-stage		3.5	n.a.	3.7	9.28
6	Two-stage	83		600	4.2	9.84
7	Two-stage	95		600	4.7	9.15
8	Single-stage		7.2	600	4.7	10.60
9	Two-stage	82		600	4.8	9.60
10	Two-stage	80		600	5.6	10.44
11	Two-stage	56		600	6.4	10.59
12	Two-stage	93		570	6.5	9.46
13	Single-stage		7.2	600	7.8	10.62
14	Two-stage	73		400-600	9.9	10.55
15	Two-stage	78		400-600	11.1	10.16
16	Two-stage	75		500	12.9	10.27
17	Two-stage	83		400-600	15.1	9.45

n.a. Not available

TABLE 10

EFFECT OF GRINDING UO_2 POWDER ON THE DENSITY OF SINTERED PELLETS

Duration of Grinding, hr.	Density of Sintered Pellets, g/cm^3	Sintering Temperature °C	Concentration of Iron Impurity in UO_2, ppm
0	9.45	1500	40
2.5	10.05	1600	n.a.
4.5	10.46	1600	600
21	10.72	1600	> 1000

n.a. Not available

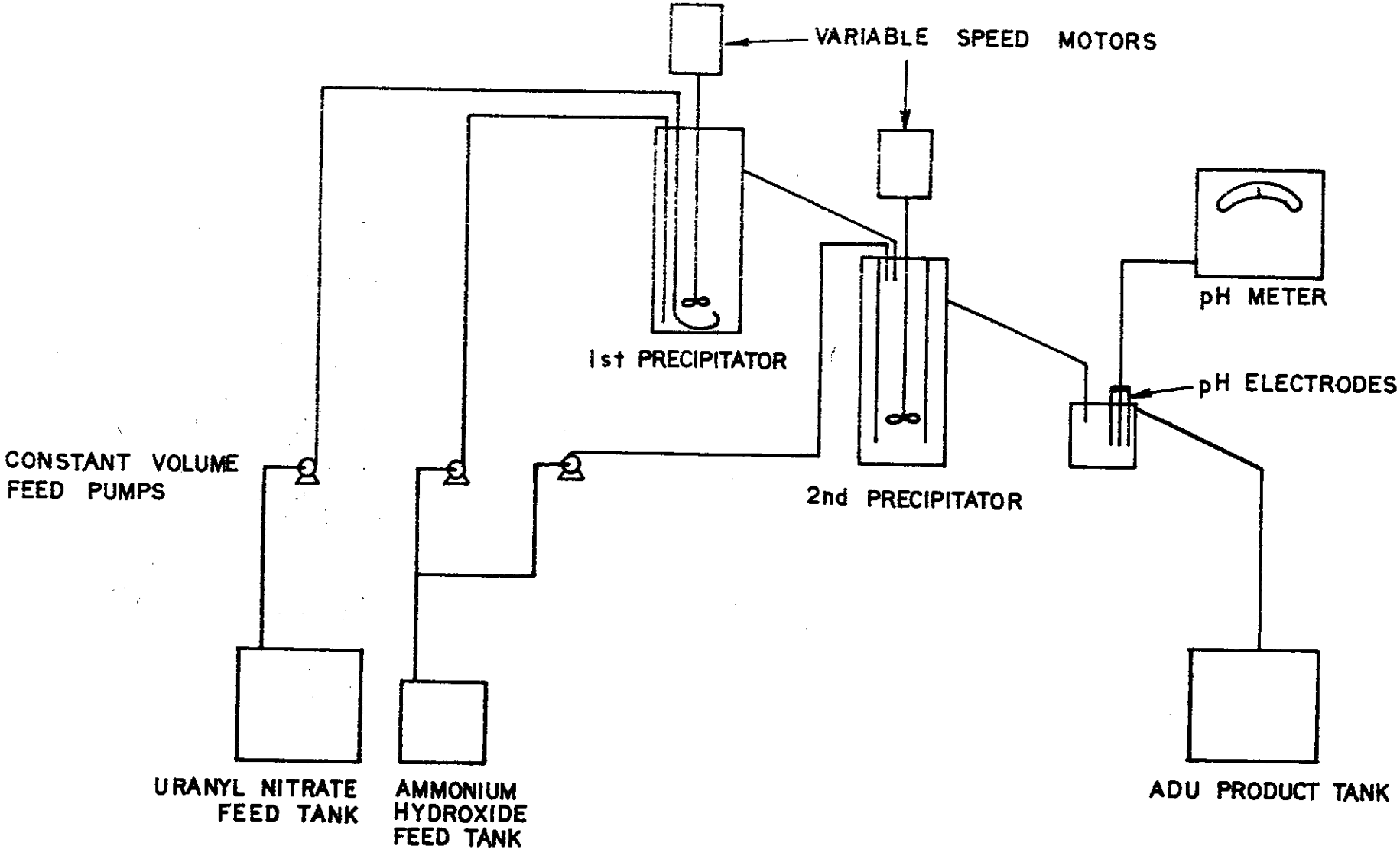


FIGURE 1. ADU PRECIPITATION EQUIPMENT

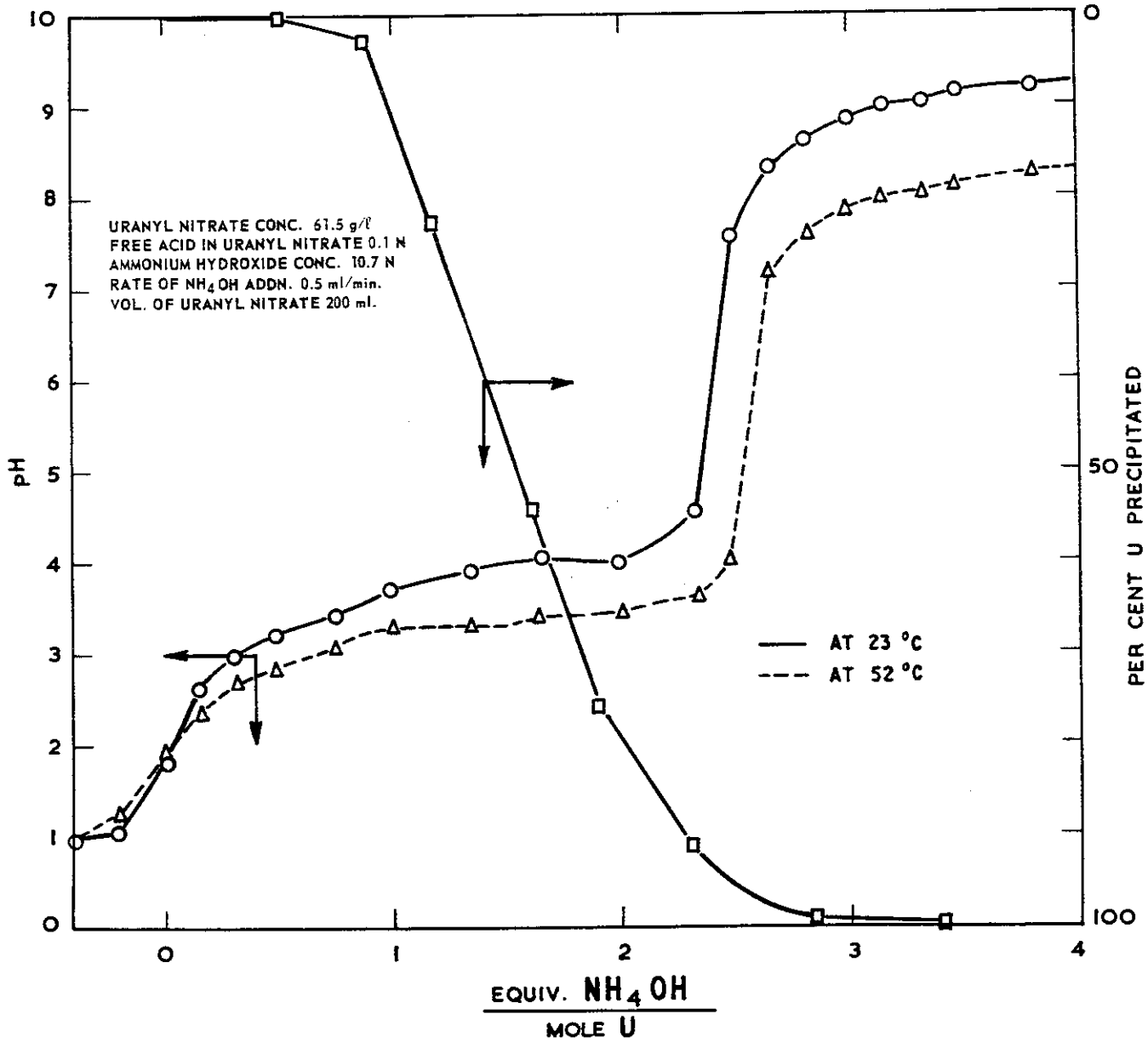
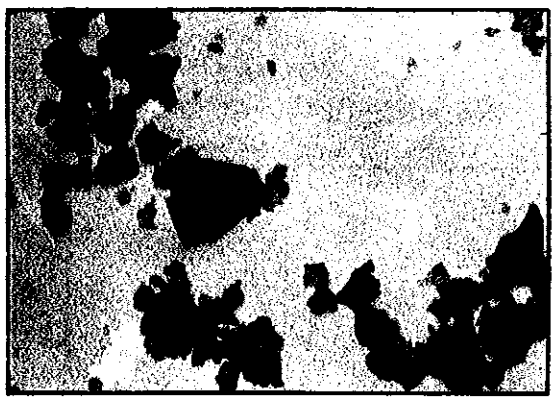


FIGURE 2. TITRATION DATA FOR URANYL NITRATE — AMMONIUM HYDROXIDE



X40,000

FIGURE 3. ADU CRYSTALLITES PRECIPITATED AT pH 3.5

X40,000

FIGURE 4. ADU CRYSTALLITES PRECIPITATED AT pH 7.0

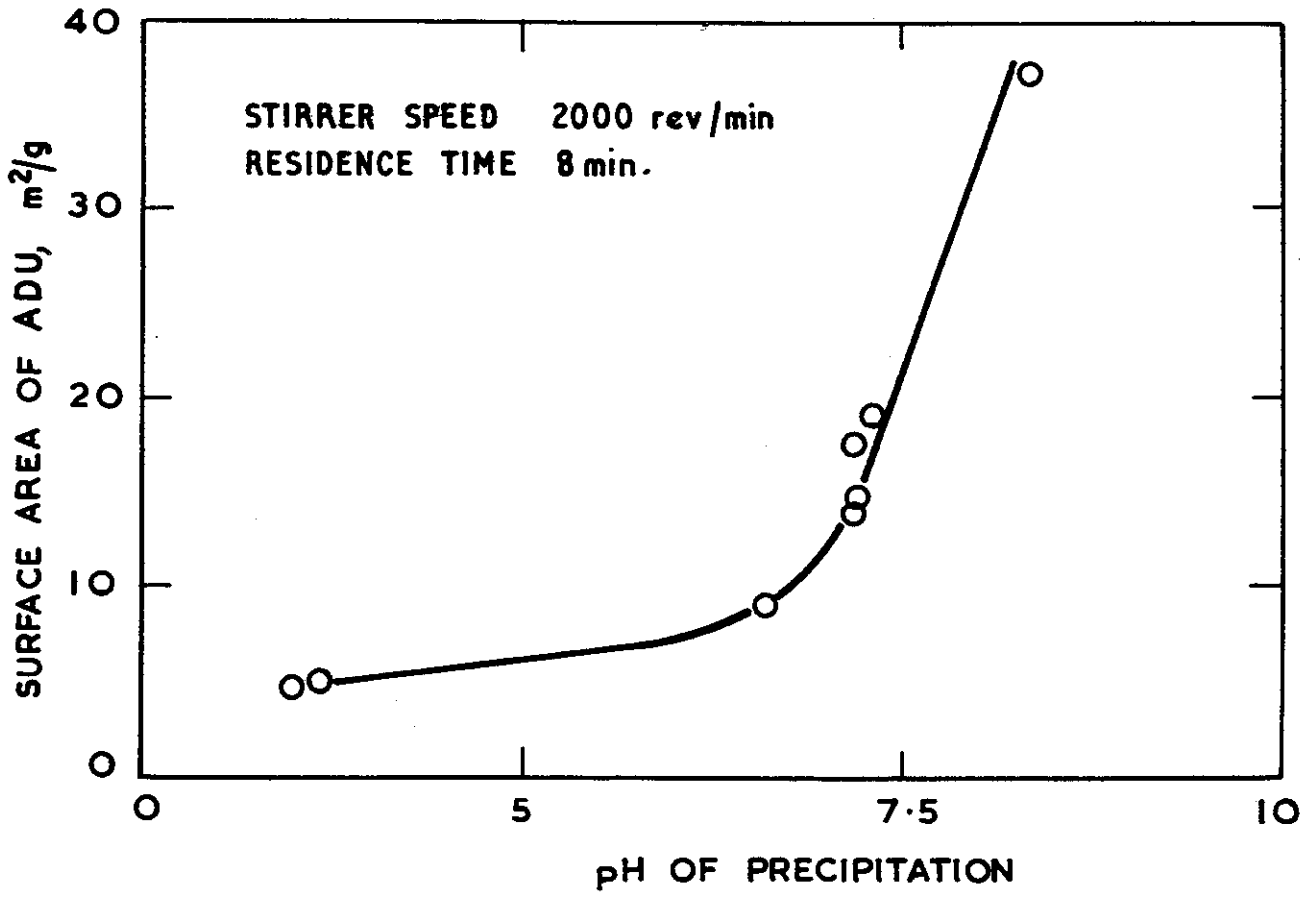


FIGURE 5. DEPENDENCE OF ADU SURFACE AREA ON pH OF SINGLE-STAGE PRECIPITATION

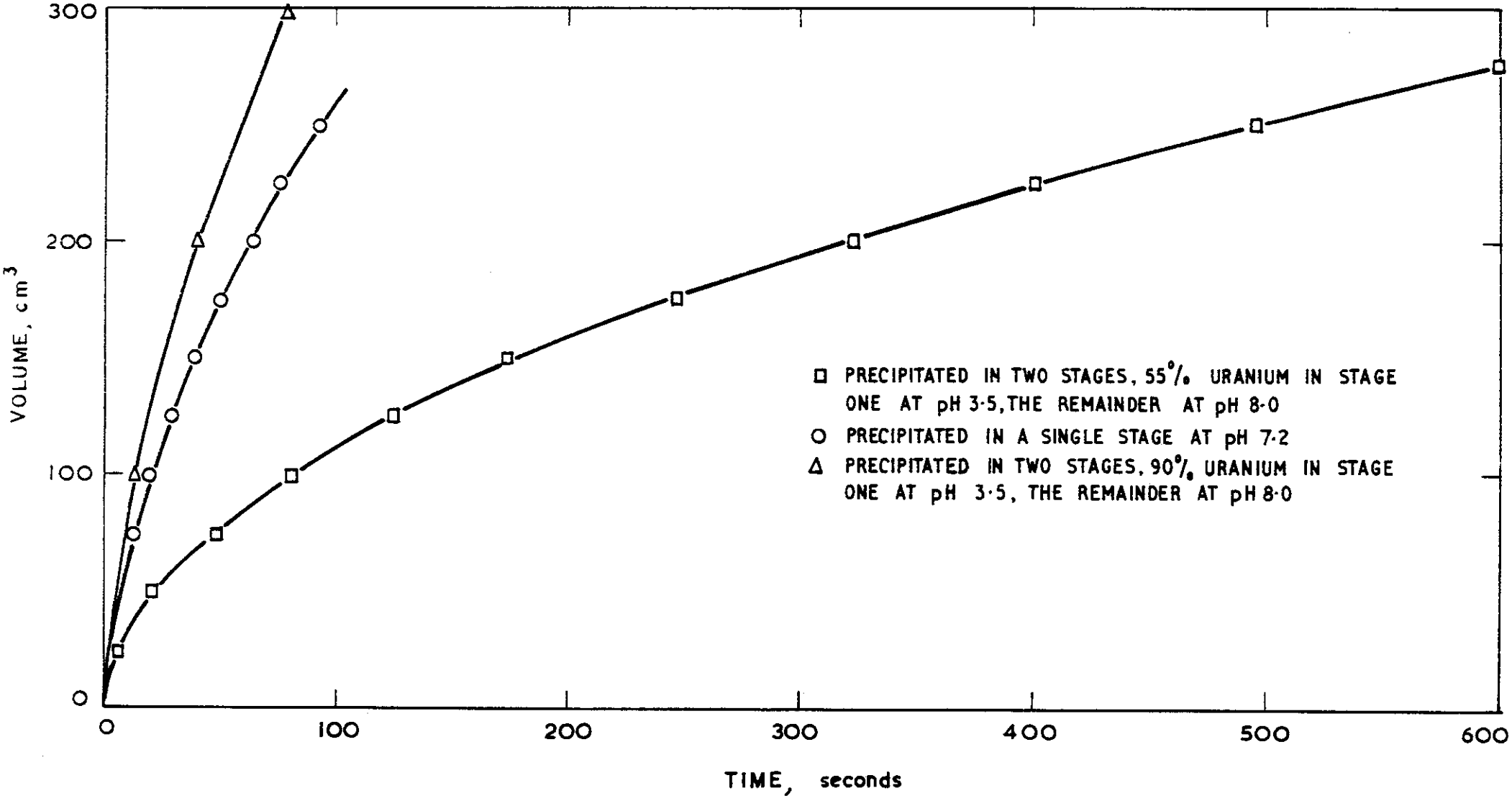


FIGURE 6. TYPICAL FILTRATION DATA (VOLUME OF FILTRATE v. TIME)

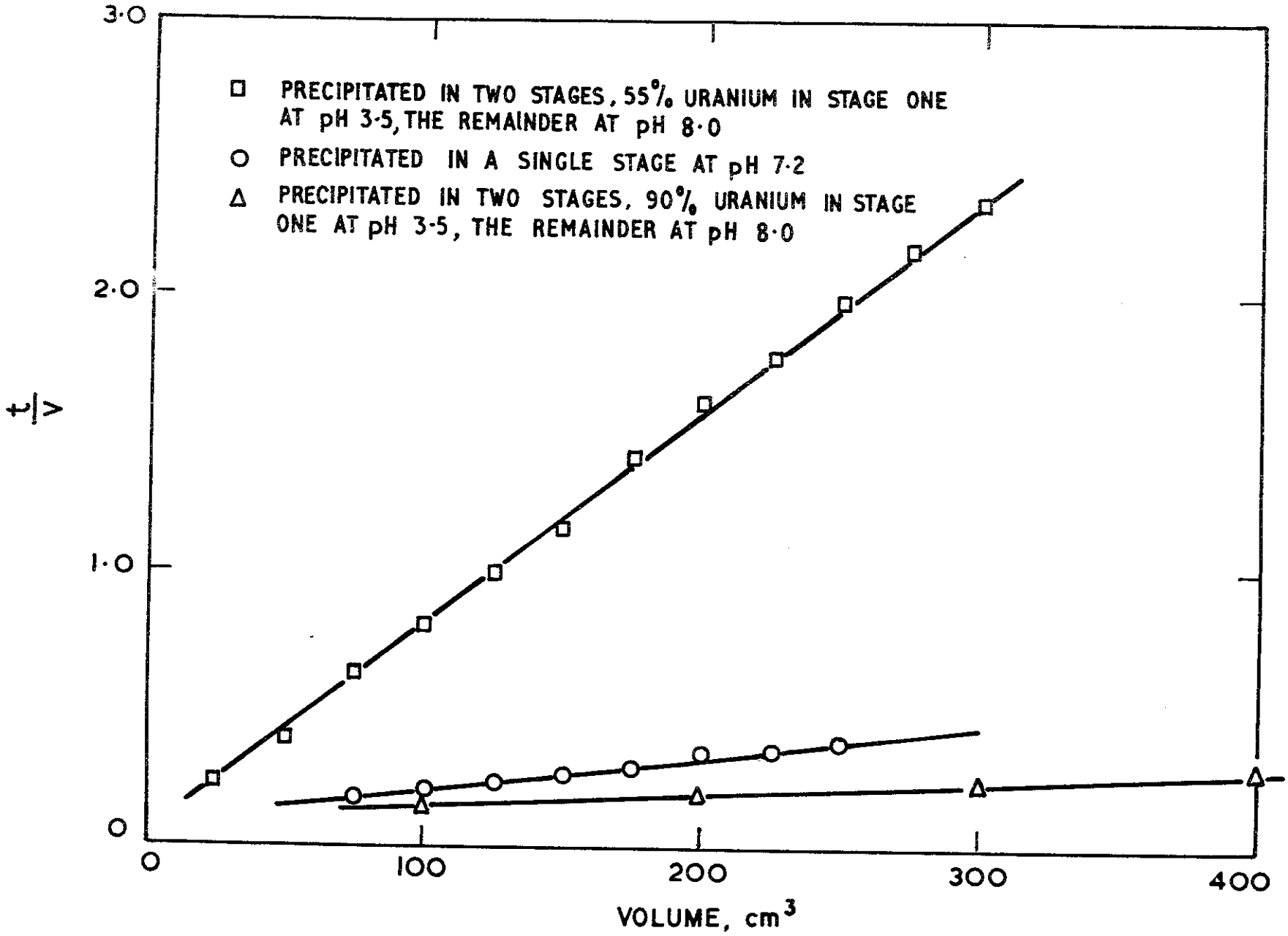


FIGURE 7. TYPICAL FILTRATION DATA (VOLUME OF FILTRATE v. $\frac{t}{V}$)

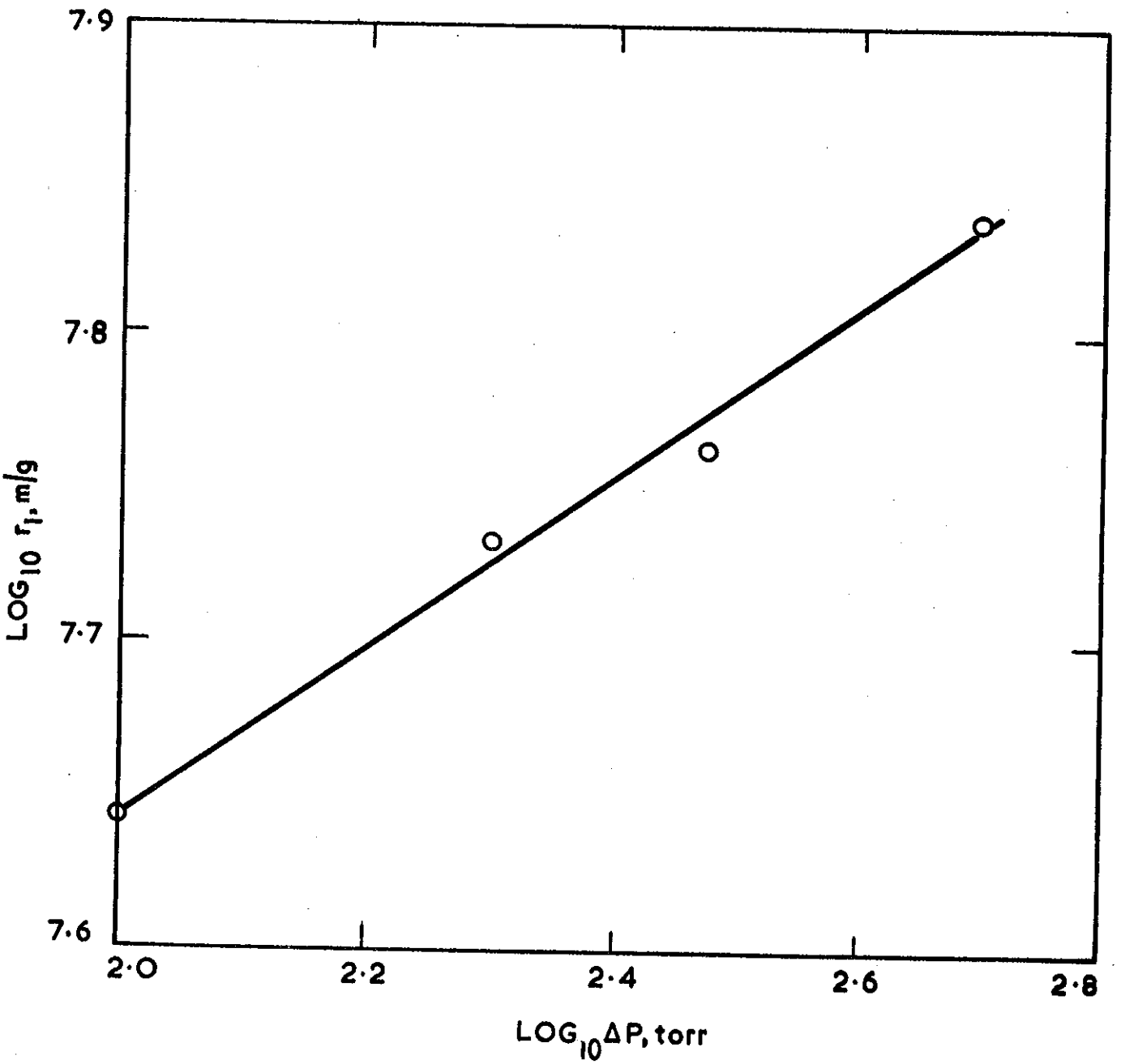


FIGURE 8. VARIATION OF SPECIFIC FILTRATION RESISTANCE WITH PRESSURE

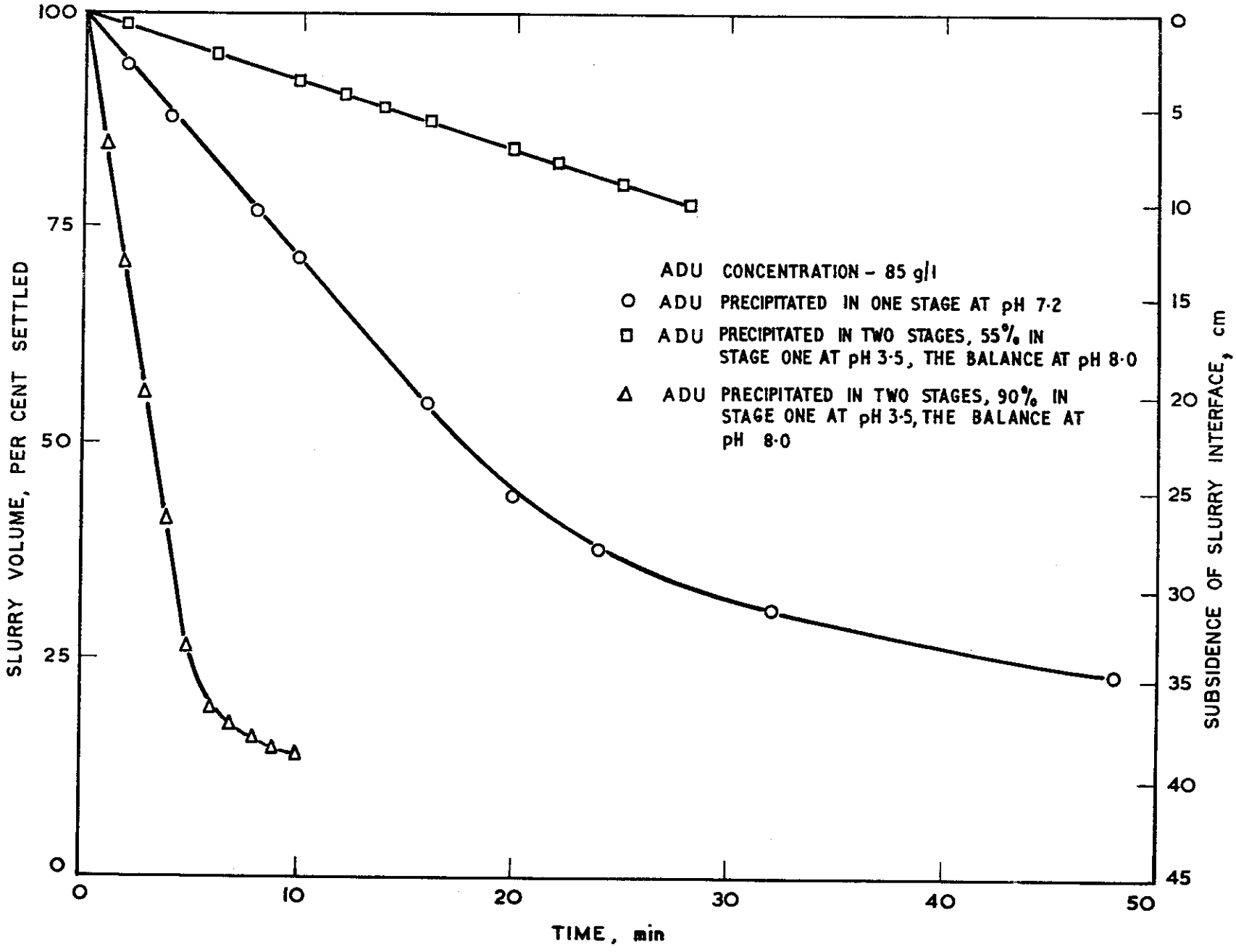


FIGURE 9. TYPICAL ADU SLURRY SETTLING DATA

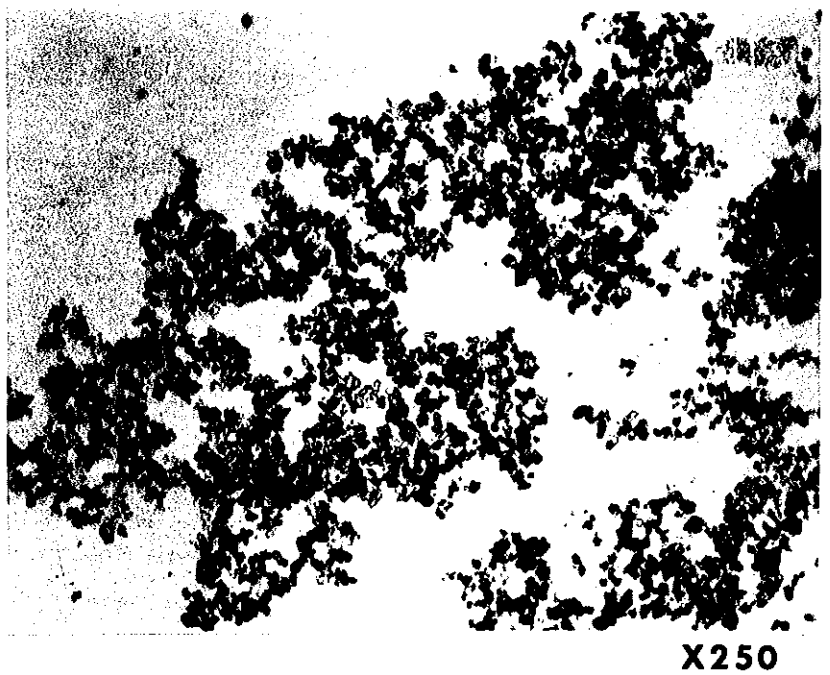


FIGURE 10. ADU AGGLOMERATES PRECIPITATED AT pH 7.2

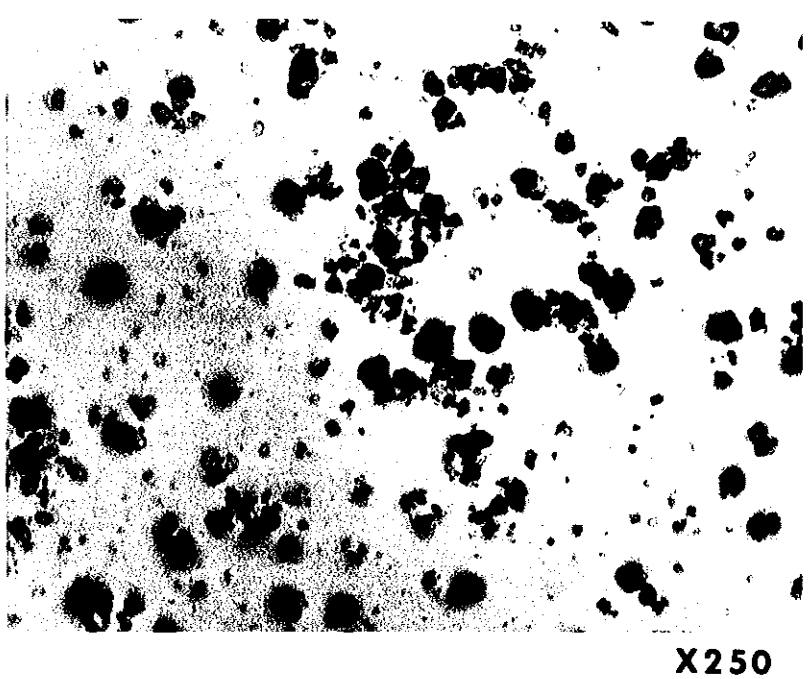


FIGURE 11. ADU AGGLOMERATES PRECIPITATED AT pH 3.5

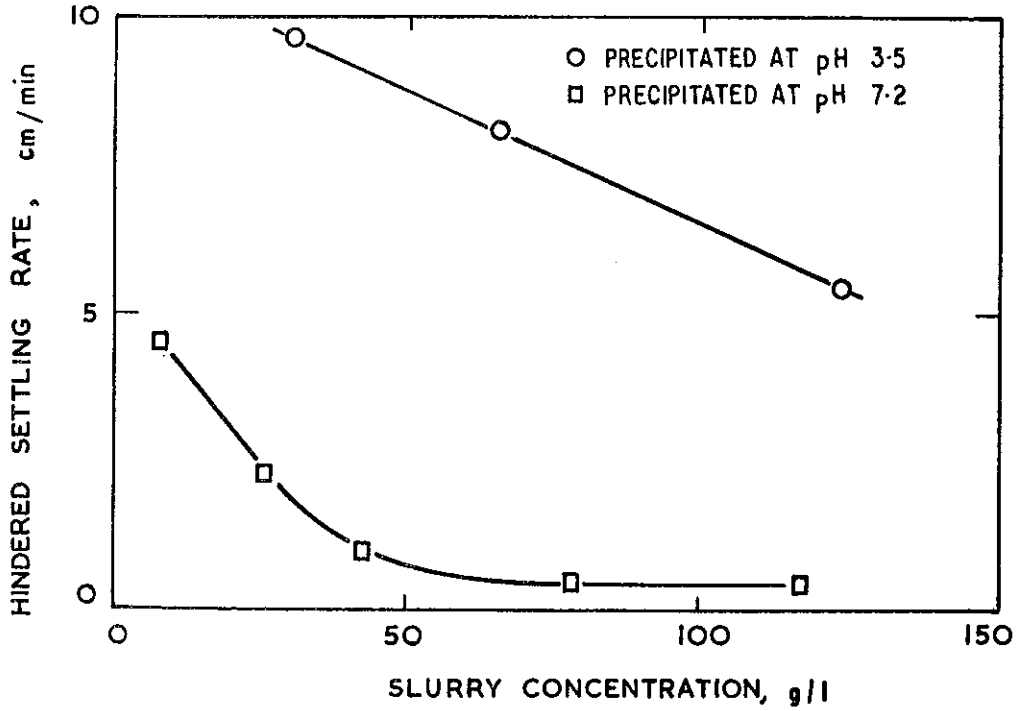


FIGURE 12. EFFECT OF SLURRY CONCENTRATION ON HINDERED SETTLING RATE OF ADU

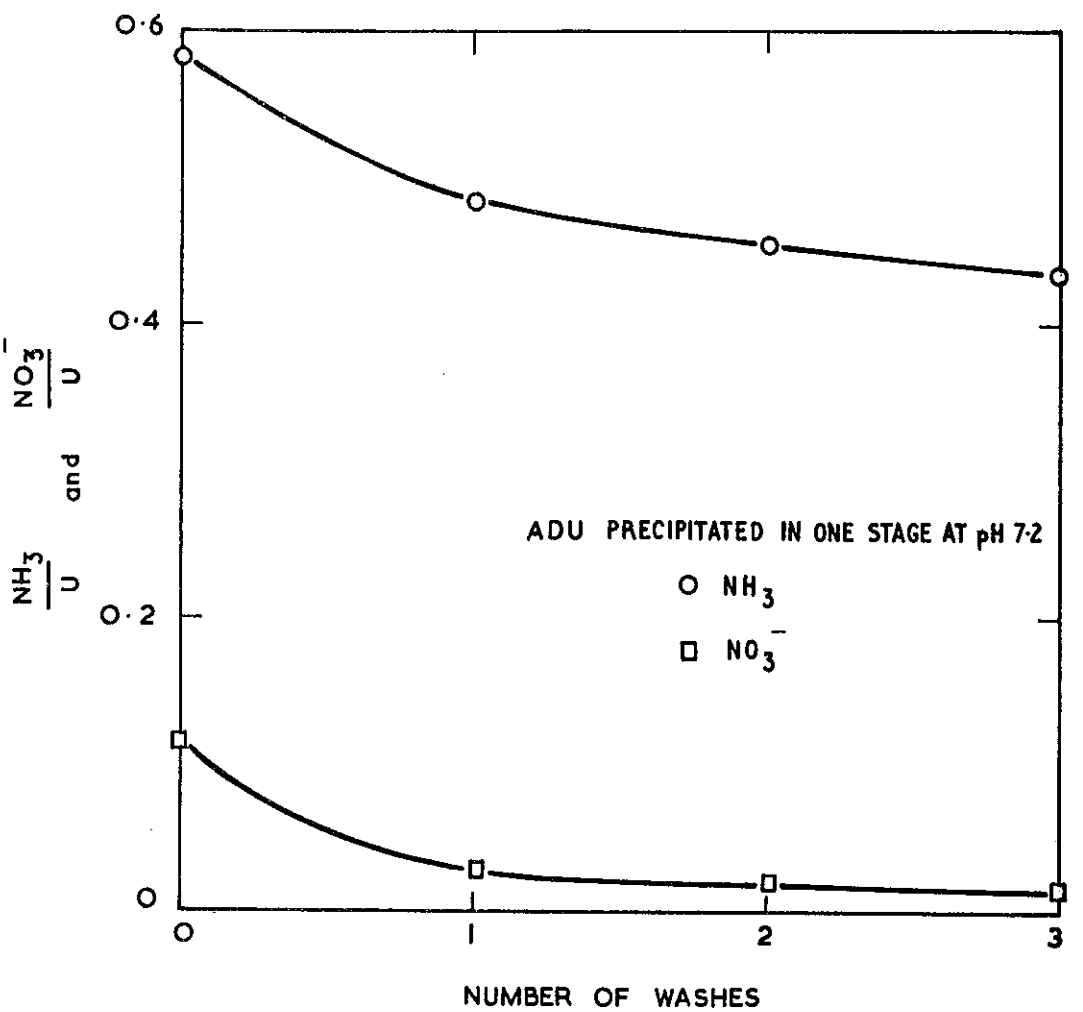


FIGURE 13. EFFECT OF WASHING ON CHEMICAL COMPOSITION OF ADU

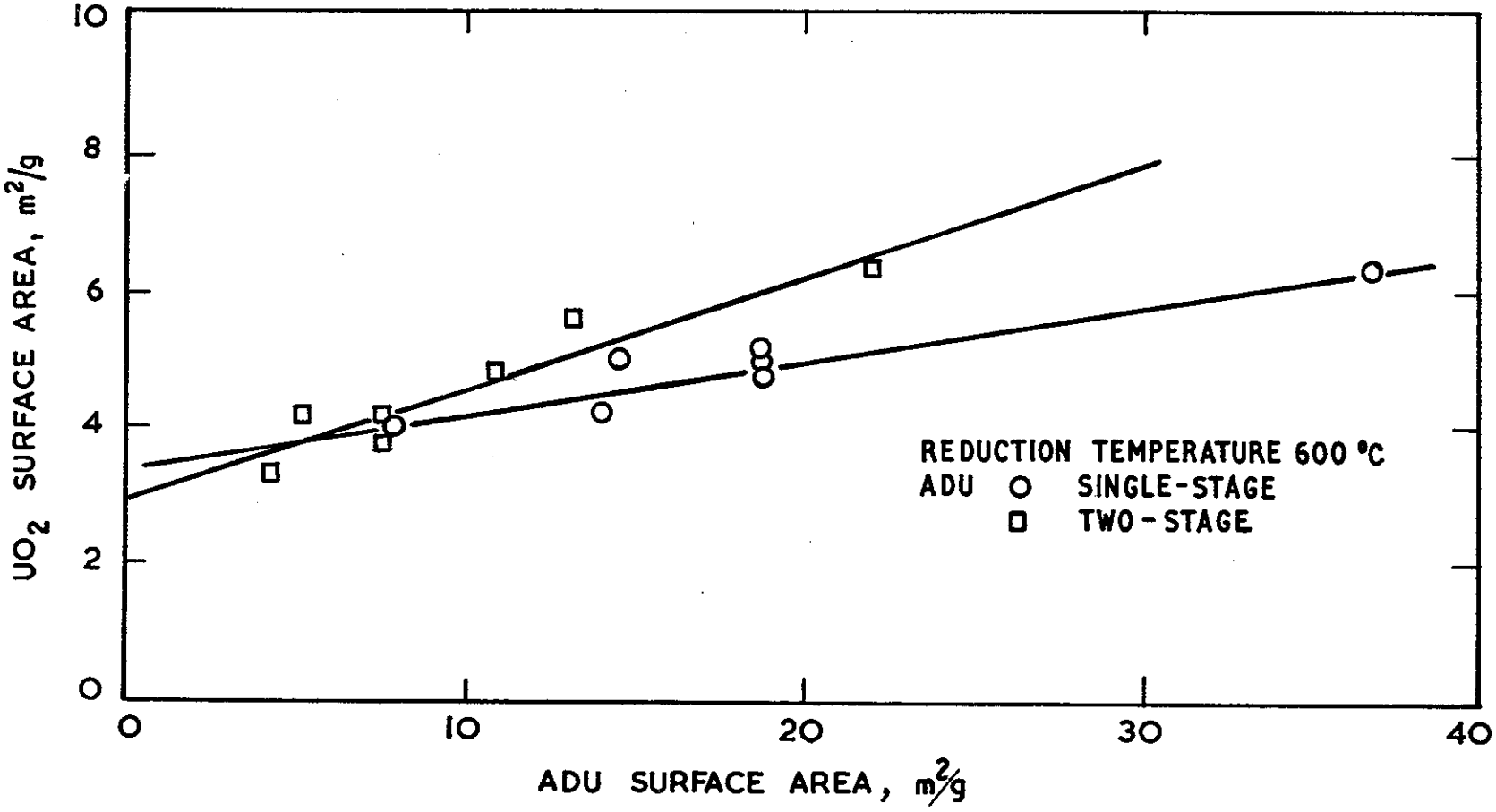
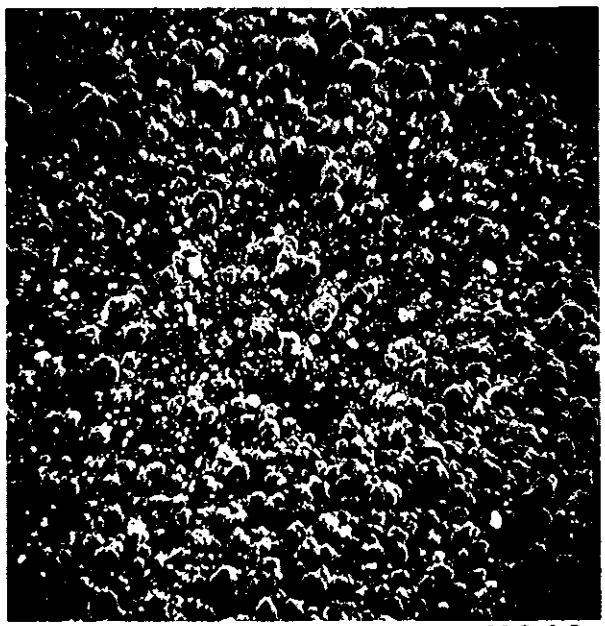
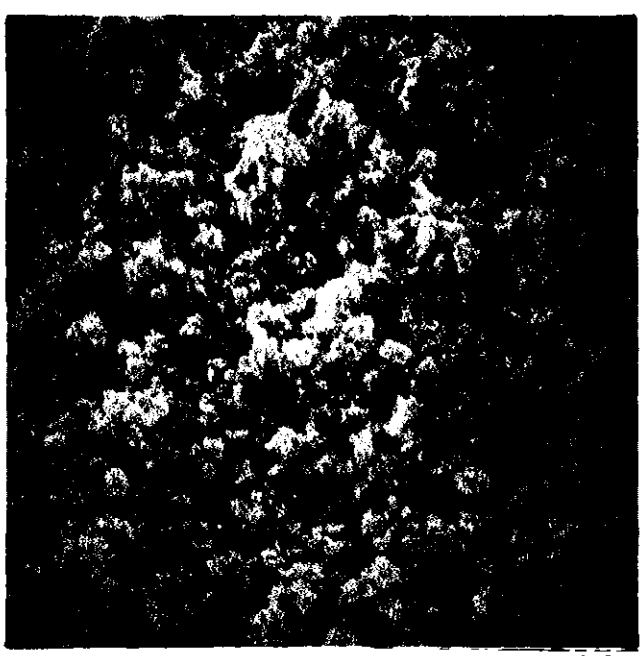


FIGURE 14. UO_2 SURFACE AREA AS A FUNCTION OF ADU SURFACE AREA



X240

FIGURE 15. UO_2 POWDER PRODUCED FROM ADU CONTAINING LARGE AGGLOMERATES



X2,400

FIGURE 16. UO_2 POWDER PRODUCED FROM ADU PRECIPITATED AT pH 7.2

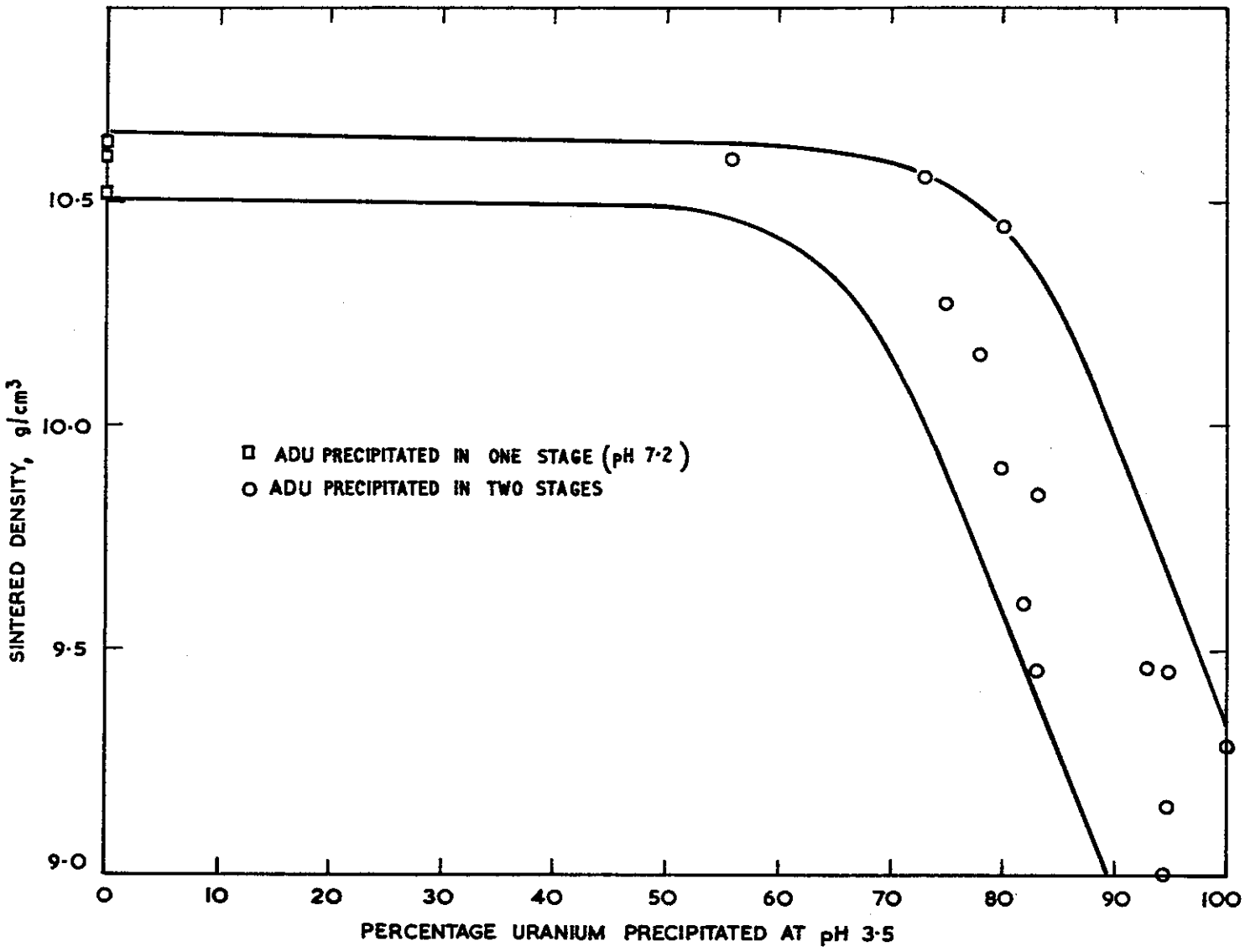
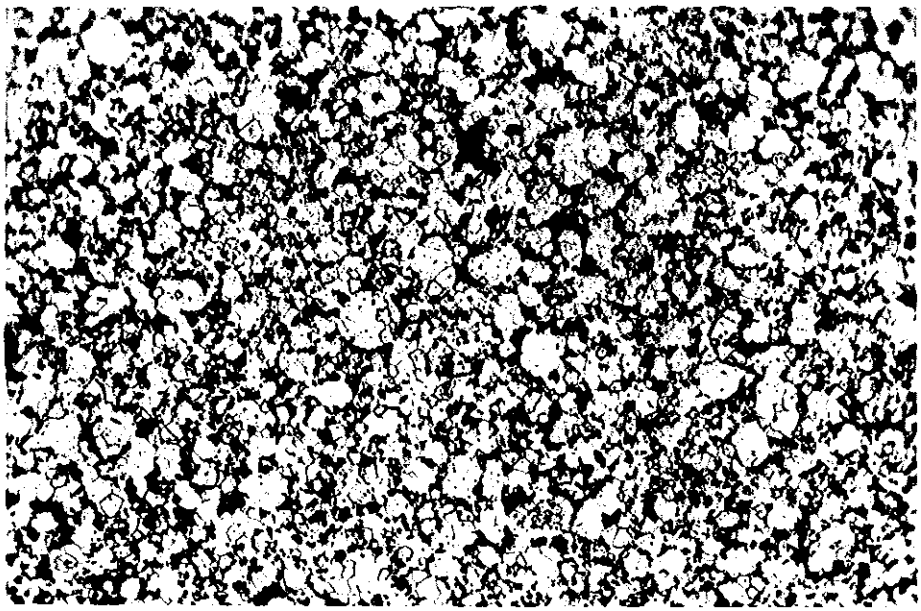
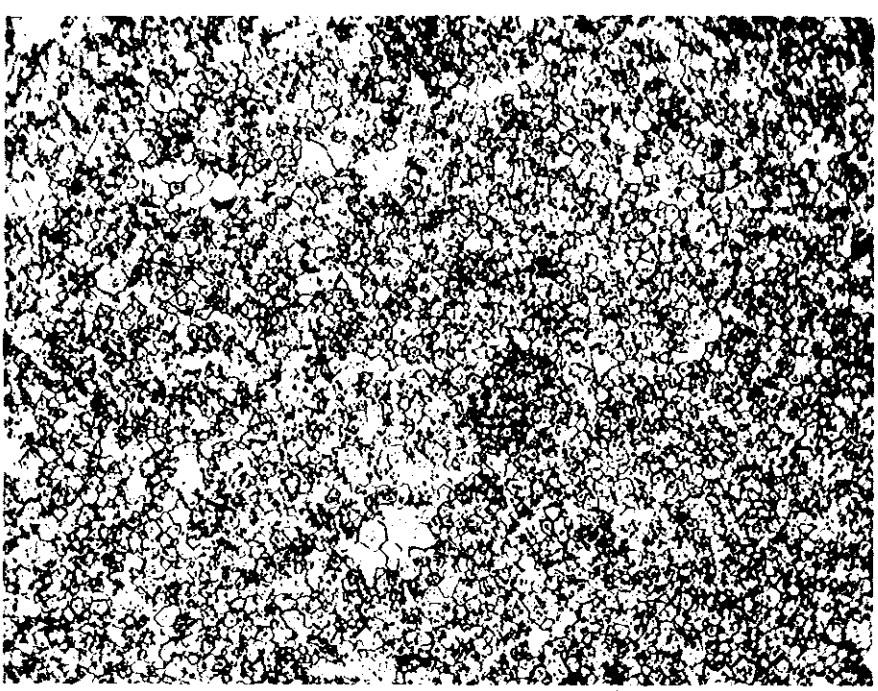


FIGURE 17. PERCENTAGE URANIUM PRECIPITATED AT pH 3.5 v. SINTERED DENSITY OF DERIVED UO_2 PELLETS



X500

FIGURE 18. ETCHED POLISHED SECTION OF UO_2 PELLET NUMBER 12, TABLE 9



X500

FIGURE 19. ETCHED POLISHED SECTION OF UO_2 PELLET NUMBER 8, TABLE 9