

PRECIPITATION OF AMMONIUM DIURANATE - A STUDY

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The precipitation of Ammonium diuranate (ADU) forms the first step in the production of UO_2 fuel for our reactors, and hence the quality and consistency of the ADU precipitate is very important in industrial operations. An investigation, on the precipitation of ADU, was carried out under conditions similar to those in industrial production, to evaluate the effect of various variables on the consistency and the quality of ADU. The variables studied were concentration of uranium & ammonia, pH, temperature and form of ammonia (gas or solution). The properties studied were the settling rate of the precipitates, surface area of the ADUs and calcined oxides and compositional characteristics of the ADUs. Multifactorial experiments and ruggedness tests were applied to identify the parameters to which the precipitation process is most vulnerable, so that such parameters may be controlled effectively. Besides, the effect and the importance of equilibrium conditions during the precipitation process, on the quality of the final ADU, was also established. The paper presents the results of these studies and arrives at the best precipitation conditions.

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* Since retired.

INTRODUCTION

In the production of UO_2 fuel pellets, the precipitation of ammonium diuranate (ADU) forms the first step. This is followed by drying and calcination of the ADU, and subsequent hydrogen reduction to UO_2 followed by stabilisation, pelletising and sintering.

There are several variables in the ADU precipitation, which affect the consistency of the precipitate which, in turn, may possibly be carried forward, contributing to the final inconsistency in the finished pellets.

Investigations were carried out, on a laboratory scale, to generate information regarding the ADU precipitation to obtain 'consistent' ADU. The parameters studied were the concentrations of uranium and ammonia, pH, temperature of precipitation, form of ammonia (solution or gas) as well as the effect of washing the precipitates. The effect of precipitating under equilibrium and nonequilibrium conditions were also investigated. The properties measured were the settling rates of ADU precipitates, surface area of the ADUs and the calcined oxides and composition of the ADUs. Precipitation studies were made in a batchwise manner under conditions which are close to those ⁱⁿ operating plants.

These investigations were aimed at identifying the parameter/parameters to which the measured properties are most vulnerable so that they can be controlled effectively.

This paper describes the experimental approach, the results and the inferences that can be drawn.

EXPERIMENTAL

Reagents and apparatus:

Stock solution of uranyl nitrate (about 100 g of uranium/L).
Ammonia: Sarabhai M Chemicals GR (density - 0.91, 25% W/W) was freshly diluted, as and when required and standardised. All the other reagents are of analytically pure grade.

1. pH meter: Elico digital pH meter, model LI-120 along with Elico glass and calomel electrodes.
2. Magnetic stirrer: Cenco make, with adjustable control.
3. Spectrophotometer, Hitachi - Model 330.

4. Surface Area Analyser, fabricated in Analytical Chemistry Division, BARC, based on the physical adsorption of nitrogen gas, at liquid nitrogen temperature, in a dynamic mode from a continuously flowing mixture of nitrogen and hydrogen; uses a thermal conductivity detector for measuring the adsorption and desorption along with a built-in electronic integrator.

Analytical Methods:

1. All the ADU precipitates were dried in an air oven at 105°C for 4 hours (unless otherwise specified) and preserved in a desiccator.

2. Uranium in the ADUs were estimated by the peroxide colorimetric method at 420 nm.

3. Ammonia was determined by steam distillation, after addition of sodium hydroxide, collecting in hydrochloric acid of known strength and back titrating with standard alkali (Kjeldahl's method).

4. Nitrate in the samples was determined by reduction with Devarda's alloy, followed by steam distillation of ammonia as in 3 above.

5. The surface area of the ADUs as well as the oxides obtained after calcination were measured in the surface area analyser.

RESULTS AND DISCUSSION

1. Multifactorial experiments and Ruggedness Tests:

A ruggedness test, similar to the one suggested by Youden¹ and used by Sarkar and Sankar Das² was adopted in the initial sets of experiments on the study of the precipitation conditions of uranium. The idea behind the ruggedness test is to make a deliberate, simultaneous change in the specified conditions and to ascertain whether the method (process, here) is sensitive to such changes and if sensitive, to identify the one to which the method is most vulnerable. Much labour can be saved by using an 'efficient plan' to single out those factors (variables) affecting the results. In one such multifactorial 'package', seven variables can be investigated with just eight experiments². In another, three variables with just four experiments can be used, as was done in the following

sets of experiments. The efficiency comes from the fact that each of the four experiments is used three times. Out of the three identified variables, the effect of one of the variables at two 'chosen levels' is examined. The design of the experiment is such that the two levels of the other two variables are changed in such a way that their effect is nullified in the pairs chosen. The use of averages increases the chance of detecting any effect on the result as a consequence of the change in the specified condition.

1.1. Table I gives the details of the four experiments involving three conditions (concentration of uranium: 100 or 60 g/L; concentration of ammonia: 10 or 8N; and pH : 3.3 or 7). In each case, to 250 ml of uranium solution, maintained at a constant temperature of 50°C (+ 1-2°C), ammonia was added at a constant rate of about 0.5 ml/min. with constant stirring. After the precipitation, the stirring was stopped and the settling rate of the precipitate layer was noted down.

1.1.1. Youden's ruggedness test (Table II) shows that the difference in the settling time due to the variation of pH is the highest and the effect of variation in pH on the settling behaviour of ADUs far outweighs the effect of variation in the concentration of either uranium or ammonia.

These two pH values of 3.3 and 7 were chosen because the first one corresponds to that pH region in which the bulk of the precipitation takes place (plateau region) and the second, viz. pH 7 corresponds to the end of precipitation. Apparently the role of the concentrations is only minor in comparison to pH. Low pH slurry is very sluggish in settling compared to the high pH slurry. Low pH slurries will, thus, be decidedly troublesome in their settling behaviour.

1.1.2. On drying at 105°C, all these precipitates caked. Though six of them were soft cakes, which easily crumbled to powder on pressing in a glass rod, the two precipitates formed at pH 3.3 and were dried without washing yielded comparatively hard cakes (clinker type). This is also reflected in the surface area values which are given in column 6 and 7 of Table I.

When the precipitates are unwashed and dried, pH has the maximum effect on the surface area as brought out by the ruggedness test (Table II). This is essentially due to the formation of hard cakes from the lower pH slurries leading to lower surface areas. When precipitates are washed this effect seems to disappear. In industrial operation, formation of such clinkers from low pH slurries, may not be desirable, as in the subsequent stages these clinkers may introduce thermal gradients during drying and decomposition.

These precipitates were calcined by slow heating to 670°C and surface area measurements were made on the oxides also. These results are also included in Table I (columns 8 and 9). It is interesting to note that after gradual and slow decomposition, the oxides, in all these cases end up with more or less same surface area. However, it should be borne in mind that these results are based on small samples heated at a slow and constant rate of 10°C/min. This will not be the case in plant operation, where heating is quicker and far less uniform, in addition to the cakes being thick. These factors may have a great role in producing powders of differing surface areas in the plant.

1.1.3. Tables III and IV summarise the data on the composition and the ruggedness test on the compositions of these precipitates. The unwashed precipitates contain around 6-9% ammonium nitrate, which as expected, was reduced on washing. In all the unwashed precipitates, the NH_3 to U mole ratios are all around 0.4 (Table IV). The yellow cake is usually referred to^{as} ammonium diuranate (ADU). For a stoichiometric formula of $(\text{NH}_4)_2\text{U}_2\text{O}_7$, the NH_3 :U ratio should be 1. However, no ratio reaching even 0.5 was observed in these experiments. Eburns and Watson³ had reported, as early as 1958, that the yellow precipitate called ADU can have NH_3 :U ratio varying from 0.3 - 0.5, depending on the pH of the supernatant liquid and the amount of washing the precipitate receives. They also reported that it can further lose ammonia when dried above 105°C. Colborn et al⁴ have reported that the molecular structure of ADU is generally assumed to be represented as

$(\text{NH}_4)_2\text{U}_2\text{O}_7$ or $(\text{NH}_4)_2\text{U}_4\text{O}_{13}$ or combination of these. Deptula⁵, in a study of the composition of ammonium uranates, observed that $\text{NH}_3:\text{U}$ ratio varied from about 0.2 - 0.5 as pH increased. No ratio higher than 0.5 could be obtained by him. Our results in Table IV confirm these earlier observations. The yellow cake, though commonly called as diuranate, is basically a non-stoichiometric compound of variable composition. It is doubtful whether reproducible chemical composition is achievable at all and hence is of no use as a parameter for either academic characterisation or for control purposes. Within these limitations, no composition difference was noticeable in the unwashed precipitates due to the variant conditions. When the precipitates were washed, there was a decrease in $\text{NH}_3:\text{U}$ ratio, as expected. While there is loss of ammonia in all the cases due to washing, there is a minor indication that the precipitates formed at the lower pH of 3.3 seem to lose ammonia faster than the ones at pH 7. This can be seen from the actual mole ratios and also from the ruggedness test (Table IV). In view of the above, it may be more appropriate to call these cakes as ammonium polyuranates rather than diuranates.

1.2. The initial set of experiments showed that concentration of uranium and ammonia have only minor effect, whereas pH has decidedly a greater influence on the precipitates. In view of this initial finding, the concentrations of uranium and ammonia were fixed at about 100 g/L and 10N respectively for subsequent experiments. Attention was paid to a narrower range of pH 6 and 8 (on either side of pH 7), in the next set of multivariant experiments. Table V gives the experimental conditions. The temperature of precipitation was chosen as the second variant (50°C and room temperature of 25°C). The third variant was the form of ammonia used - 10N ammonia solution or gaseous ammonia. As before, the stirring and the rate of addition of ammonia solution were constant. Where ammonia gas was used, about 30-50 bubbles/minute, through an orifice of 3-4 mm diameter, was maintained.

1.2.1. The settling times, in this set of experiments, are also given in Table V (column 5). None of the three variables viz. pH

(in this range), temperature of precipitation or form of ammonia have any marked effect on the settling times as shown by the ruggedness test for settling time (Table VI). Of the three, the temperature has the least effect. pH as well as ammonia have somewhat similar but marginally higher effect.

1.2.2. The three variants in these experiments do not influence the surface area of the unwashed precipitates in a significant manner (Table VI). However, it is seen that the influence of temperature is marginally more than that due to the other two. Precipitation from warm solutions gives a product of marginally higher surface area. When the precipitates are washed, pH has the maximum effect on the surface area as is dramatically brought out by the ruggedness test (Table VI). As pointed out in the earlier set of experiments, ammonia is lost from the precipitate on washing. When the pHs of the water washings were actually measured in this set, the pH increased with each successive washing, going to greater than 9 pH in the case of the precipitates obtained at pH 8. Apparently this results in increased surface area of the precipitates.

As in the earlier set, the ADUs were decomposed and the surface area of the oxide residues are given in Table V (column 8 and 9). The oxides of all the washed precipitates tend to reach a surface area of about $5 \text{ m}^2 \text{ g}^{-1}$ and all the unwashed ones to about $6 \text{ m}^2 \text{ g}^{-1}$. In one case (experiment VIII), the ADU was heated to about 960°C instead of 650°C , and in this case the surface area dropped considerably to $1.4 \text{ m}^2 \text{ g}^{-1}$. Thermal analysis indicated that though the weight remained constant after about 650°C (indicating no change in the composition), the D.T.A. baseline showed a gradual and continuous endothermic change in this region of $650\text{--}960^\circ\text{C}$ (Figure 1). Considering that the surface area at the end has fallen to $1.4 \text{ m}^2 \text{ g}^{-1}$ from about $6 \text{ m}^2 \text{ g}^{-1}$, it is reasonable to correlate these two and infer that at temperatures above 650°C , a sintering process of the oxide starts.

2. EQUILIBRIUM CONDITIONS IN THE PRECIPITATION PROCESS

The multifactorial experiments showed that of all the parameters studied, pH is the most decisive one. The type of composi-

tions obtained by us, as well as by the earlier workers, show that U:NH₃ ratio is much higher than would be expected on stoichiometric basis, indicating the presence of polymerised uranium species in the precipitates. This leads us to the possibility of non-attainment of equilibrium as a factor to be looked into. Deptula⁵ had earlier made a potentiometric study using about 25 g/L uranyl nitrate solution and 0.2 N ammonia solution. Using concentrations close to those employed in our plants (100 g/L), we carried out potentiometric titrations of uranyl solutions against ammonia. To 50 ml of uranyl nitrate solution, 10N ammonia was added and this titration was followed potentiometrically. Fig. 2 gives the potentiometric titrations. Curve A represents the case where after every incremental addition of ammonium hydroxide, the mixture (which was constantly and vigorously stirred) was allowed to come to pH equilibrium before the next addition. Generally the time required was of the order of 5-10 minutes for each addition. Hence about 15 minutes was allowed at every point. Curve B represents the titration in which ammonia was added at a constant arbitrary rate while the uranium solution was stirred continuously. The titration for curve B took far less time than that for curve A. Curve A and B can be taken to represent equilibrium and non equilibrium conditions respectively.

Titration under equilibrium conditions (Curve A) shows that there is an initial rise in pH upto a value of about 3, during which the neutralisation of the free acid takes place. Also, possibly, some polymerisation of the uranyl ion may be taking place simultaneously without precipitation (darkening of the colour to brownish yellow from the initial greenish yellow). This is followed by a plateau region at about pH 3.3 - 3.4, during which ADU is precipitated continuously and gradually. Ammonia is consumed for the precipitation of ADU without any rise in pH during this stage, after which there is an inflexion point followed by a sudden rise from 3.5 to a pH region of 7-8 indicating no reaction during this sudden jump. The pH tends to taper off slowly after this jump, around a pH of about 9-10. It was noticed that the precipitate at this stage became coarse, granular and tended to settle faster even during the

titration.

When ammonia was added under non-equilibrium conditions (Curve B - faster constant addition), after the initial increase in pH due to free acid neutralisation, the pH rose gradually but continuously to a value of about 5.5, around which it fluctuated in a zig-zag manner, before shooting up parallelly to the other curve, from pH 6 onwards.

Under equilibrium conditions, the precipitation takes place at a constant lower pH whereas under non-equilibrium conditions, the plateau region is narrower, zig-zag and is higher by about 2.5 pH units. Curve A (equilibrium) is such that it can be expected to be reproduced, whereas the curve B (non-equilibrium) will be more difficult to reproduce. If the rate of addition is decreased and/or the mixing is more thorough, the curve B will approach the equilibrium curve A and vice-versa.

Our experimental observations, are very similar, though not exactly identical to that of Deptula⁵. His plateau region was closer to pH 4.2, needed far more time to reach equilibrium at the start of precipitation (30-100 minutes) and the dip in his pH value at the start of precipitation was far more pronounced (about 1 pH unit). All these differences can easily be attributed to the differences in concentrations employed.

Based on these curves, the following could be inferred about the *operation* of plants.

- 1) In the first stage upto pH \sim 3, free acid will get neutralised
- (2) In the second stage (which is supposed to operate in the pH range 3-5), the way the ammonium hydroxide is added and mixed, will play a great role in deciding the type of precipitation. If non-equilibrium conditions prevail, the quality of the product could be non-reproducible. It is felt that some of the non-reproducibilities - particularly the settling/nonsettling nature of the precipitates obtained can be rationalised through the above laboratory observations.

2.1. Influence of pH and equilibrium on the Settling Rates of

the ADUs:

Based on the above observations that when precipitation is made close to the equilibrium, and that the precipitates so formed at pH about 9 are coarser and granular, the following experiments were carried out to arrive at the best precipitation conditions.

To 100 ml of the uranium solutions (100 g/L), 10 N ammonium hydroxide was added from a burette with constant vigorous stirring, with the pH being monitored constantly. The slurry at the end of each experiment was transferred to a 100 ml measuring cylinder (ID about 30 mm), and the sedimentation rates were measured. Figure 3 records the settling curves.

In the first instance, the pH was raised to about 6.5 under equilibrium conditions (incremental addition - about 2-3 hrs) left aside for about 30 minutes and the settling rate measured (1a, Fig.3). After measuring the settling rate, this slurry was retransferred to the original beaker and the pH was raised further to 9, and the settling rate was measured again (curve 1b). These two curves dramatically bring out the steep improvement in the settling rate on raising the pH to about 9. The settling rate is nearly five times faster than that obtained for the product at pH 6-7.

In the next experiment, a constant rate of addition of ammonia, of 1 ml/min. (as against incremental addition) was maintained and the pH raised to 6.5 in about 20 minutes. It was noticed that the pH remained close to about 3.3 during precipitation, i.e. still close to equilibrium. It was left at pH 6.5 for about an hour and then pH was raised to 9 (settling curve 2). This curve is close to 1b indicating that it is possible to work close to equilibrium using constant rate of addition. Curve 3 represents the case where pH was raised directly to pH 9 (but slowly and working close to equilibrium in about 20 minutes) with no interruption at about pH 6.5. This curve is also close to the other two curves, though slightly on the higher side. This particular slurry at pH 9 was left aside for another hour, was restirred and the settling rate

remeasured. There was no appreciable difference - i.e. allowing extra time at pH 9 does not additionally contribute to any improvement in the settling rate.

When the pH was raised directly to 9 by addition of ammonia solution in a very fast manner in a few minutes (i.e. under non-equilibrium conditions, the slurry was found not to settle at all (Curve 4). Curve 5 represents a modification of Curve 4: the pH was raised very fast in a few minutes in a non-equilibrium way to pH 6.5 instead of to 9, but allowed to stand for about 100 minutes at this pH, to allow a chance to reach equilibrium (pH fell to 5.8). The pH was subsequently raised to 9. This curve is close to curve 4, showing the importance of the 'plateau - equilibrium stage'. Two more experiments (curves 6 and 7) were repeated on separate days, similar to curves 1 and 2 and these confirm the above data. They also show the consistently good settling behaviour of these precipitates. At pH 9, the initial steep portion of the settling curves works out to be in the region of 4 cm/min. as against less than 1 cm/min at pH 6-7. Besides, at pH 9, there are no fines floating after the settling. Our data on settling curves is also in conformity with those of Deptula⁶ who used 10 g/l uranium concentration and about 1N ammonia.

The best results, for settling, are obtained when the slurry pH is raised to 9 instead of leaving it at pH 6-7. However, it is essential that the raising of the pH, from the beginning, should be gradual and close to the equilibrium plateau region. Abrupt addition of ammonia or sudden rise in pH should be avoided.

The ammonium nitrate content of the ADU s produced at pH 9 were in the region of about 10%. It was found possible to reduce this to about 3%, by decanting the supernatant liquor, repulping with dilute ammonia a couple of times and discarding the supernatant each time. The settling rate continued to be the same after the first two washings (Curve 7).

The surface area values of ADU s produced at pH 9 corresponding to curves 2, 3, 6 and 7 of Fig.3 and the corresponding oxide residues obtained at 650°C are given in Table VII. The surface

area values, both for the ADUs as well as calcined oxides, are higher than the ones obtained earlier at lower pHs.

3. CONCLUSION

1. Ammonium polyuranate precipitated at pH 9 under conditions of pH equilibrium will give a product

- of high settling rate
- which is easily washed by decantation to remove the entrained ammonium nitrate
- of high surface area of $9-10 \text{ m}^2 \text{ g}^{-1}$ ADU (compared to the surface area of $3-5 \text{ m}^2 \text{ g}^{-1}$ as obtained at lower pH values).

2. The temperature of decomposition of UO_3 to U_3O_8 should not exceed 650°C or else there is the risk of sintering an oxide of high O/U ratio.

3. This uranate on calcination below 650°C gives U_3O_8 of high surface area of $6.5 - 7 \text{ m}^2 \text{ g}^{-1}$ (compared to the value of $4-5 \text{ m}^2 \text{ g}^{-1}$ as being obtained at low pH).

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TABLE I
Multifactorial Experiments

1	Variables			Measured property				
	2 C _U &/L	3 C _{NE} OH 4 N	4 pH	5 Settling time	6 Surface area of ADU 2 ⁻¹ m ² g	7 Washed	8 From Unwashed ADU	9 From Washed ADU
I	100	10	3.3	245	0.6 ⁺	7.9	3.9	4.0
II	100	8	7.0	38	4.2	5.4	N.D.	N.D.
III	60	10	7.0	28	7.7	5.8	4.3	4.1
IV	60	8	3.3	125*	1.6 ⁺	5.0	4.5	4.2

* Boundary was less sharp

+ Hard cakes, values are only indicative

N.D. Not determined, oxide was lost.

TABLE II

RUGGEDNESS TESTS

Variable	Values of the variable	Difference in 'D' Values		
		Settling time	Surface area of ADU	
			Unwashed	Washed
pH	7.0, 3.3	152 ^a	4.9	0.9
Concentration of uranium g/L	100, 60	65 ^b	2.3	1.3
Concentration of ammonia N	10, 8	55 ^c	1.2	1.7

a. $\frac{245 + 125}{2} - \frac{38 + 28}{2} = 152$

b. $\frac{245 + 38}{2} - \frac{28 + 125}{2} = 65$

c. $\frac{245 + 28}{2} - \frac{38 + 125}{2} = 55$

TABLE III
Composition

Expt.No.	Unwashed ADU				Washed ADU			
	I	II	III	IV	I	II	III	IV
% NH_4^+ NO_3^- in ADU	6.6	8.5	5.1	5.9	1.4	2.8	3.9	3.3
% NH_3 in ADU	1.9	1.9	2.0	2.2	1.2	1.6	1.5	1.4
% U in ADU	70.0	75.1	71.2	68.8	72.0	70.9	72.3	72.0

* Based on estimation of NO_3^- by reducing with Devarda's alloys followed by NH_3 detn.

** Corrected for NH_4^+ NO_3^- present.

TABLE IV
Effects of variables on composition

Expt.	C _U g/L	C _{NH₄OH} N	pH	Composition expressed as mole ratio of NH ₃ to U in the ADU	
				Unwashed	Washed
I	100	10	3.3	0.38	0.24
II	100	8	7	0.36	0.31
III	60	10	7	0.39	0.30
IV	60	8	3.3	0.45	0.21

Ruggedness test on composition

Variable	Difference in mole ratio due to the variable	
	Unwashed	Washed
Concn. U	0.05	0.02
" NH ₄ OH	0.02	0.01
pH	0.04	0.08

TABLE V
Multifactorial Experiments

1	Variables				Measured property			
	2	3	4	5	6	7	8	9
No.	pH	Temp °C	Ammonia	Settling time Sec/2em ht.	Surface area of diuranates $\frac{m^2}{g}$	Surface area of oxide $\frac{m^2}{g}$	from unwashed ADUs	from washed ADUs
V	6	50	Gas	57	4.9	6.0	6.0	5.3
VI	6	25	Solution 10N	36	3.2	6.2	6.0	5.3
VII	6	50	Solution 10N	52	3.7	3.7	6.2	5.3
VIII	6	25	Gas	92	3.0	2.6	1.4*	4.9

* Heated to 360°C.

TABLE VI
Ruggedness Test

Variable	Values of the variable	Settling time	Difference in 'D' values	
			Surface area of ADU	
			Unwashed	Washed
pH	8, 6	26	0.7	3.0
Temperature °C	50, 25	10	1.2	0.5
Ammonia	Gas, 10N	30	0.5	0.6

TABLE VII
Surface Area Values $\text{m}^2 \text{g}^{-1}$

Sample No.	Diuranates	Oxide residues
2	9.0	6.7
3	9.3	7.1
6	9.8	6.4
7*	10.3	7.1

* Washed ADU

Sample number corresponds to curve number of Fig.3.

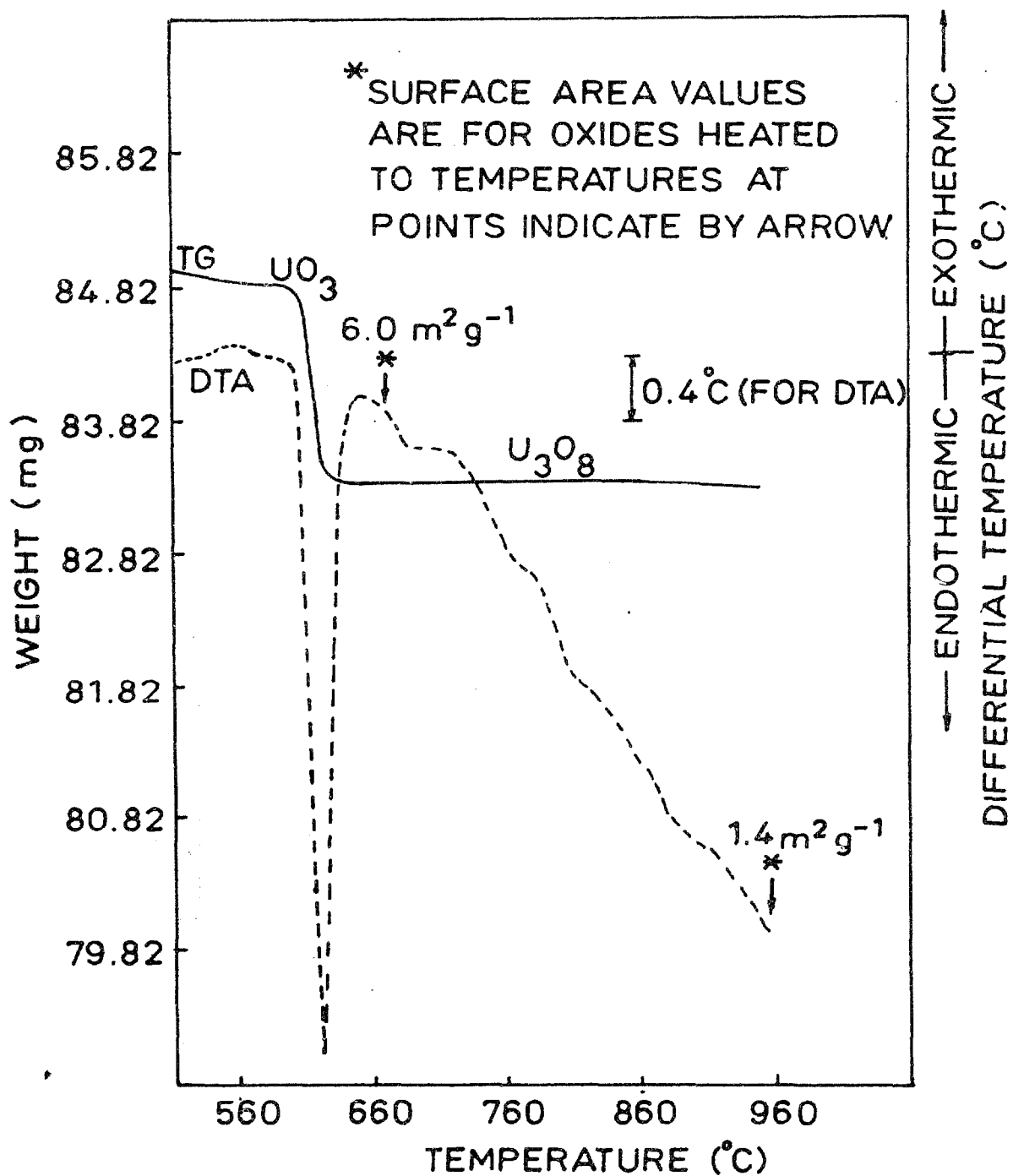


FIG. 1 SINTERING EFFECT DUE TO TEMPERATURE

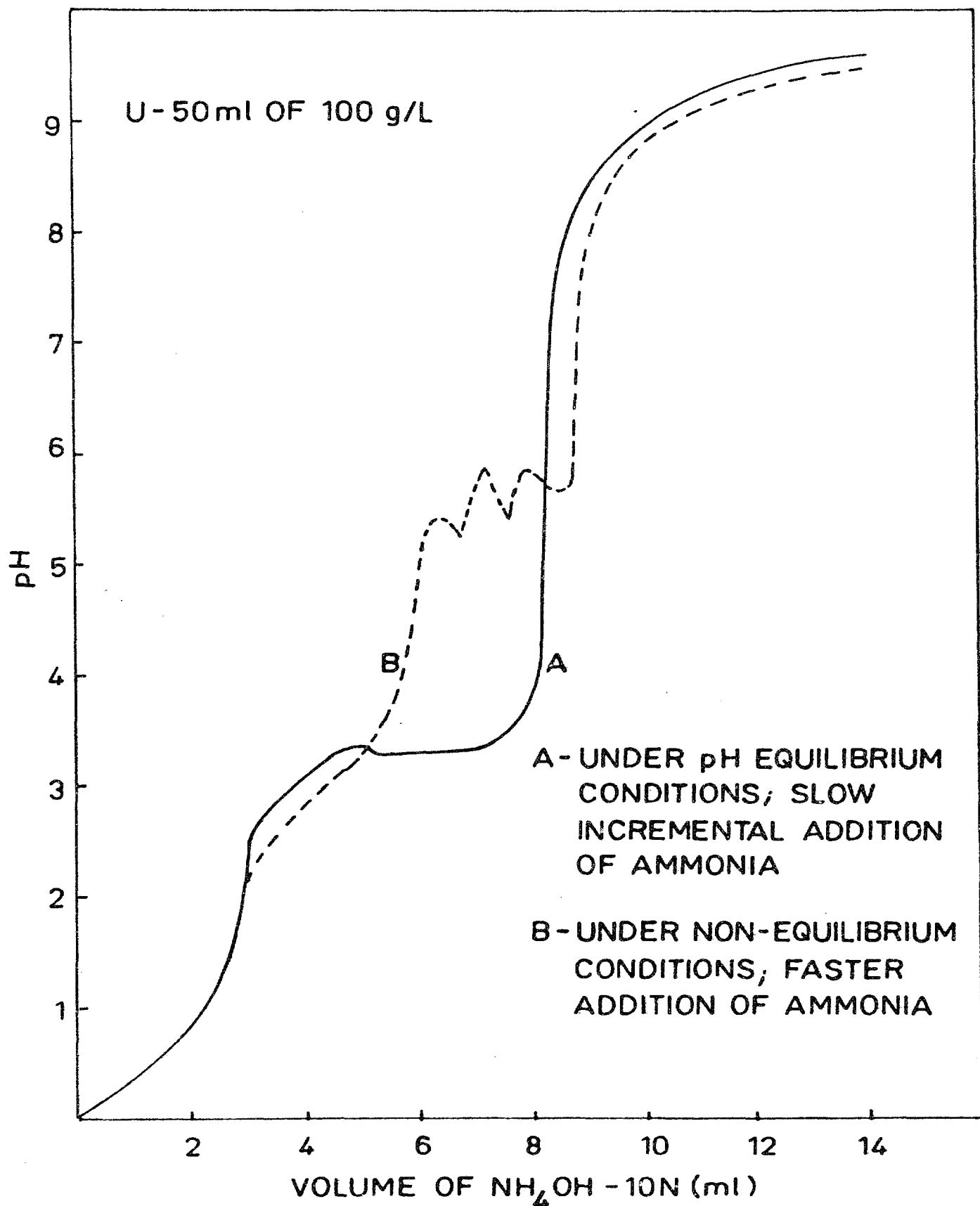


FIG. 2 POTENTIOMETRIC TITRATION

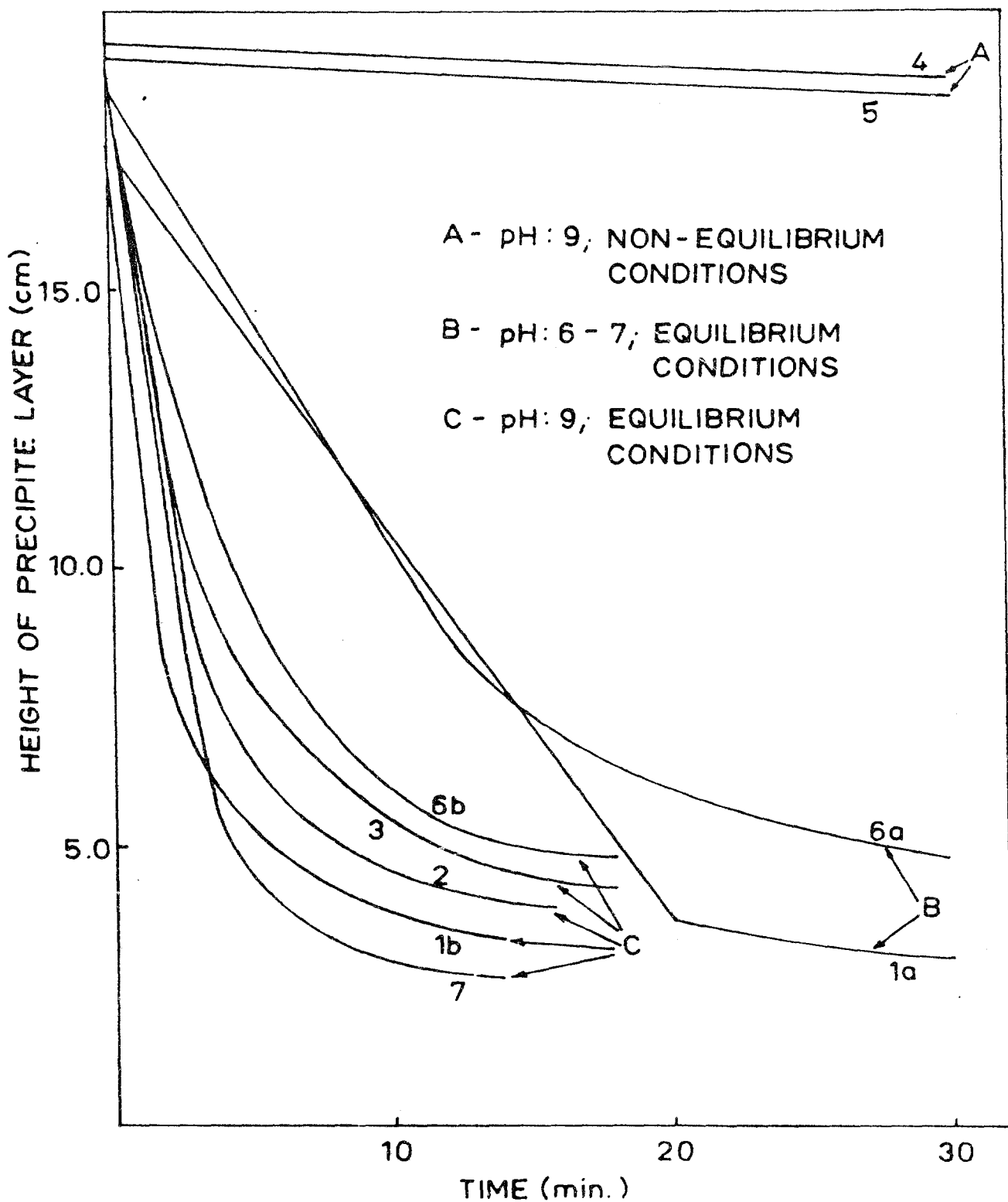


FIG. 3 SETTLING CURVES