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A SOL-GEL PROCESS FOR PREPARING ThO_2-UO_3 SOLS FROM NITRATE SOLUTIONS BY SOLVENT EXTRACTION WITH AMINES

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MASTER

OAK RIDGE NATIONAL LABORATORY
operated by
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CONTENTS

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ABSTRACT

A solvent extraction process using long-chain aliphatic amines was developed and demonstrated, on a laboratory scale, for preparing thoria sols and thorium-uranium oxide sols (containing up to 58 mole % uranium) directly from aqueous thorium nitrate--uranyl nitrate solutions. About 80 to 90% of the nitrate is extracted by contacting the solution for at least 2 min with the amine which is dissolved in an inert diluent. The aqueous phase is then separated from the organic phase and digested at least 10 min at 95 to 100°C. This converts the aqueous phase into a sol and releases additional nitrate, which is extracted with the amine in a second stage. The equilibrium nitrate: metal mole ratio decreases linearly with uranium concentration from about 0.28 for pure thoria sols to about 0.16 for thorium-uranium sols containing more than 25 mole % uranium. Most of the sols were prepared with 0.6 to 0.75 M Amberlite LA-2, an extensively branched, commercial secondary amine (N-lauryl trialkylmethyl amine) in n-paraffin or n-dodecane. Approximately 1.2 to 1.5 moles of amine per mole of initial nitrate was used to extract the nitrate. The extractions were made with the organic phase continuous at 50 to 60°C to ensure rapid phase separations.

The dilute sol may be dried to gel fragments or evaporated to a concentration of 1 to 2 M in total metal oxide and then formed into gel microspheres. The resulting fragments or spheres are dried, calcined in air at 1150°C, and finally reduced with Ar--4% H_2. Gram quantities of ceramic spheres with compositions that are currently of interest as reactor fuels were made, starting with thorium nitrate solutions that contained 17 to 26 mole % uranyl nitrate. Most of these spheres had densities greater than 95% of the theoretical densities of the oxide solid solutions, less than 1% porosity, and oxygen:uranium ratios of less than 2.01. Spheres 150 to 408 μ in diameter resisted crushing loads of 500 to greater than 2000 g.

Engineering studies of this process are now being made, using equipment that is capable of producing up to 20 kg of the mixed oxide per day.

1. INTRODUCTION

In the preparation of ceramic reactor fuels by the sol-gel technique, a hydrosol is prepared from the desired nuclear materials, converted to a gel, and densified by calcination. The hydrosol may be prepared by precipitation-peptization, dialysis, solvent extraction, or hydrothermal decomposition. The thoria sol-gel process uses the last:[1,2] thorium nitrate in solution or crystalline form is made into a dispersible oxide powder by steam denitration, and is then simply dispersed in water. Stable uranium oxide-thorium oxide sols containing up to 10 wt % uranium are formed by using uranyl nitrate, ammonium diuranate, or uranium trioxide in conjunction with the thoria sols. For uranium compositions higher than 10 wt % it has been necessary (1) to prepare thoria sols and urania sols separately and then blend them to the desired thorium: uranium ratio, or (2) to coprecipitate thorium and uranium from nitrate solution and redisperse them in water.[3,4,5] It would be desirable to find a simpler process that is capable of producing mixed sols in all useful ratios directly from thorium and uranyl nitrates. This report describes such a process, based on denitrating thorium nitrate--uranyl nitrate solutions by extraction with long-chain amines.

It is well established that amines will extract acids and metal-ion complexes from aqueous solutions.[6] In fact, amines have become important in the processing of nuclear materials[7] and have even been used to prepare colloidal suspensions (sols) of actinide metal oxides.[8,9] In one case,[8] the sols were produced by contacting thorium nitrate solutions containing 10 wt % uranyl nitrate with 10 wt % triisooctyl amine in kerosene for 3 hr at 90°C. The sol had a pH of 6.2, and 85% of the colloidal particles had diameters between 25 and 45 mμ. The nitrate:metal ratio, which is critical for calcination to dense oxide, was less important in that preparation since the sol was to remain in the liquid state. That preparation still had the disadvantage of using only 10 wt % uranyl nitrate with the thorium. The second process[9] used amines to partially denitrate thorium and/or uranium. Since too much nitrate remained in these sols for calcination to dense particles, amine was added to the dehydrating medium to extract more nitrate as the gel spheres were being formed. Thus, amines have previously been used to prepare thorium-uranium sols, but the processes did not realize the full potentialities of an amine solvent extraction process.

It is the purpose of this report to present the flowsheet for the Amine Denitration Process, in which the desired nitrate:metal ratios in mixed thorium-uranium oxide sols are achieved by extracting nitrate from the aqueous solutions with long-chain aliphatic amines. After the readily extractable nitrate is removed in the first contact, the aqueous solution is digested at 95 to 100°C to make more nitrate extractable (which is then removed in a second contact). These extraction and digestion steps can be repeated, if necessary, until a nitrate:metal ratio that is satisfactory for formation of calcinable spheres is obtained. A detailed flowsheet of the process is presented, followed by the results from studies made of the effect of various process variables on the sol product and a few tests of microsphere production. Some early single-batch extraction work that led to this process, as well as the preparation of alumina and zirconia sols by amine extraction and amine washing techniques, are described briefly in the Appendix.

2. FLOWSHEET DESCRIPTION

Thorium nitrate--uranyl nitrate solutions can be converted directly into sols by extracting the nitrate in a two-stage extraction system with long-chain aliphatic amines dissolved in a hydrocarbon diluent (Fig. 1). Sols have been prepared on a laboratory scale from solutions of $Th(NO_3)_4$ and $Th(NO_3)_4$-$UO_2(NO_3)_2$ containing up to 68 mole % $UO_2(NO_3)_2$. The aqueous solutions were contacted with an amine solution for at least 2 min, separated from the organic phase, and digested for at least 10 min at 95 to 100°C. With Amberlite LA-2, a highly branched secondary amine (N-lauryl trialkylmethyl amine), about 80 to 90% of the total nitrate was extracted in the first stage. The subsequent heating of the aqueous phase at 95 to 100°C for 10 to 30 min converted the yellow solution into a deep red sol, and released additional nitrate, which was extracted by the amine in the second stage. More than 98% of the extractable nitrate was extracted in the two stages, with the ratios of the nonextractable nitrate-to-metal ratios tending to decrease from 0.33 to about 0.16 as the mole % uranium increased from zero to 68. In addition to the nitrate removal, a small amount of water was consumed, causing a 10 to 13% increase in metal concentration in the final sol as compared with the feed solution.

The amine nitrate formed during the extraction steps is reconverted to free amine by reaction with a solution containing about 1.05 moles of sodium carbonate per mole of amine (see Fig. 2). Subsequent washing of the organic phase with water ensures that carbonate is not carried over into the extraction stages when the amine is reused in the preparation of sols.

In plant operation it may be necessary to pass the organic through a deentrainment stage prior to reconversion. Although thorium and uranium losses due to amine extraction have been very low in laboratory tests (less than 0.01 and 0.02% respectively), entrainment losses may be high enough to warrant contacting the amine phase with dilute acid or water before it is regenerated with sodium carbonate. This scrub solution may then be returned to the first extraction stage for reprocessing.

The remainder of the flowsheet (Fig. 1), comprising the microsphere formation and calcining stages, has been demonstrated on a laboratory scale with the thorium-uranium mixtures that are currently of interest as ceramic reactor fuels. These sols, containing about 17 to 26 mole % uranium, were evaporated to give final sols that were 1 to 2 $\underline{M}$ in total metal. The latter sols were formed into microspheres by injection as droplets into a dehydrating medium consisting primarily of 2-ethyl-1-hexanol. The gelled spheres were dried, calcined in air at 1150°C, and finally reduced with Ar--4% H_2 to yield a satisfactory ceramic product. As a typical

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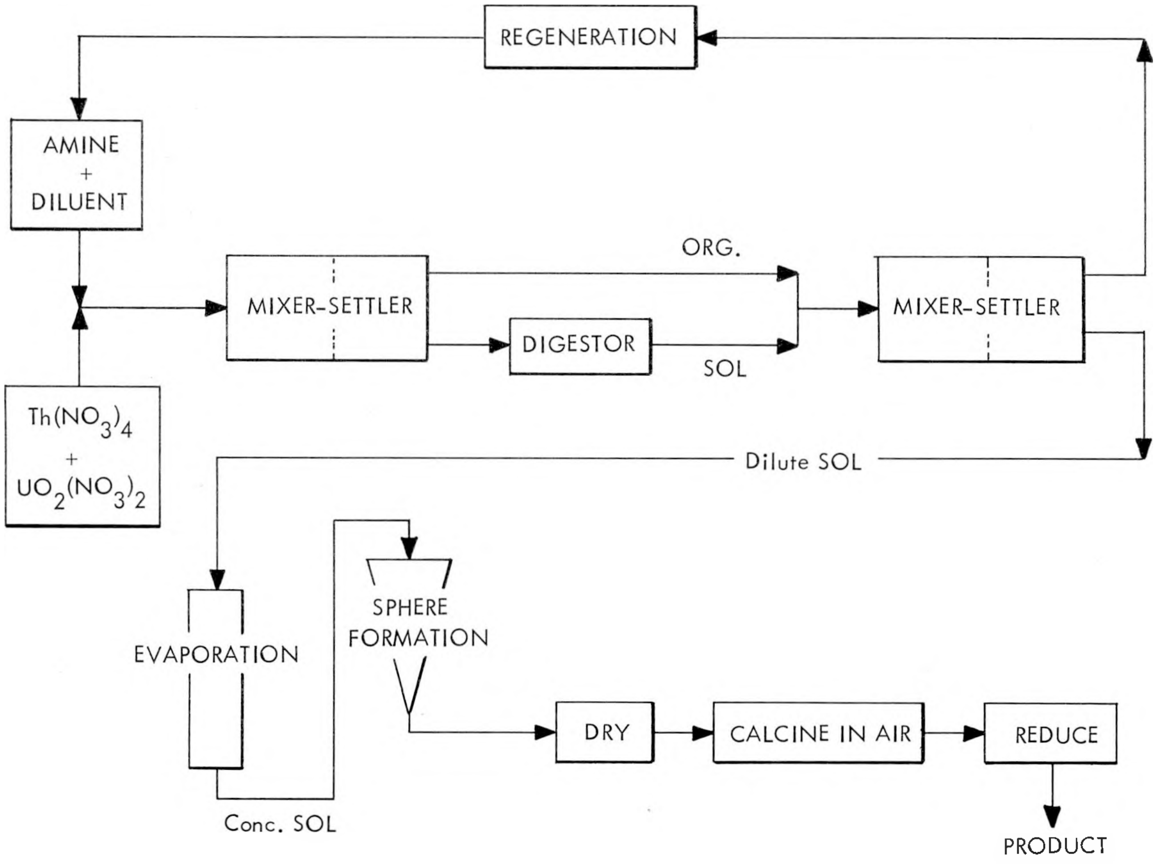

Fig. 1. Amine Denitration Process.

example, a sol that was about 0.3 M in Th + U was evaporated to give a final sol that was 1.10 M in thorium, 0.32 M in uranium, 0.30 M in nitrate, and 0.01 M in carbon of an unspecified form. Spheres were formed by injecting this sol into 2-ethyl-1-hexanol containing 0.5 vol % H_2O and suitable surfactants. The gelled spheres were dried overnight at 100°C, held at 170 to 180°C for about 5 hr, and then calcined in air at 1150°C. The resulting spheres were shiny black and had an oxygen-to-uranium ratio of 2.003. Porosity was less than 1%, and the density was greater than 95% of the theoretical density of the oxide solid solution. Individual spheres 150 to 350 μ in diameter resisted crushing forces of 940 to 2000 g.

Engineering-scale studies of this process are now being made with equipment that is capable of producing up to 20 kg of the mixed oxide per day. A rate of about 15 kg per day was attained using the flowsheet shown in Fig. 2.[10] This particular flowsheet uses 50% excess amine for the nitrate extraction and 20% excess Na_2CO_3 in the regeneration step. All the extractions are made at 50 to 60°C, whereas the digestion is carried out at 95 to 100°C. The third extraction stage was included to give maximum efficiency in the nitrate extraction after the digestion step. In the preliminary runs the sol product had a nitrate:metal ratio of about 0.1, which is somewhat lower than the values achieved in laboratory tests.

3. STUDY OF VARIABLES

Earlier workers observed that the nitrate:metal ratio is one of the more critical factors determining the ability of a sol to form acceptable microspheres.[11] Therefore, investigations were aimed chiefly at determining what effect changes in flowsheet conditions would have on the final nitrate:metal mole ratio in the sol. Preliminary work indicated that sols with a nitrate:metal mole ratio of about 0.2 would produce satisfactory microspheres, depending on the column conditions (see Section 5).

The analytical accuracy obtainable in evaluating the nitrate:metal ratios is of concern in these tests. Repeated analyses of a single batch of sol, over a two-month period, indicated that the limit of error in replicate nitrate determinations was not more than ± 20% at the 95% confidence level. The 18 to 26 determinations for each component averaged as follows:

Th - 42.94 mg/ml
U - 15.33 mg/ml
Kjeldahl NO_3^- - 3.16 mg/ml
Colorimetric NO_3^- - 3.09 mg/ml
pH - 4.30 to 3.95 (decreasing with time)

The limits of error (applicable to single-determinations) for the thorium and uranium were satisfactory, ± 1.2 and ± 2.9%, respectively, at the 95% confidence level. The

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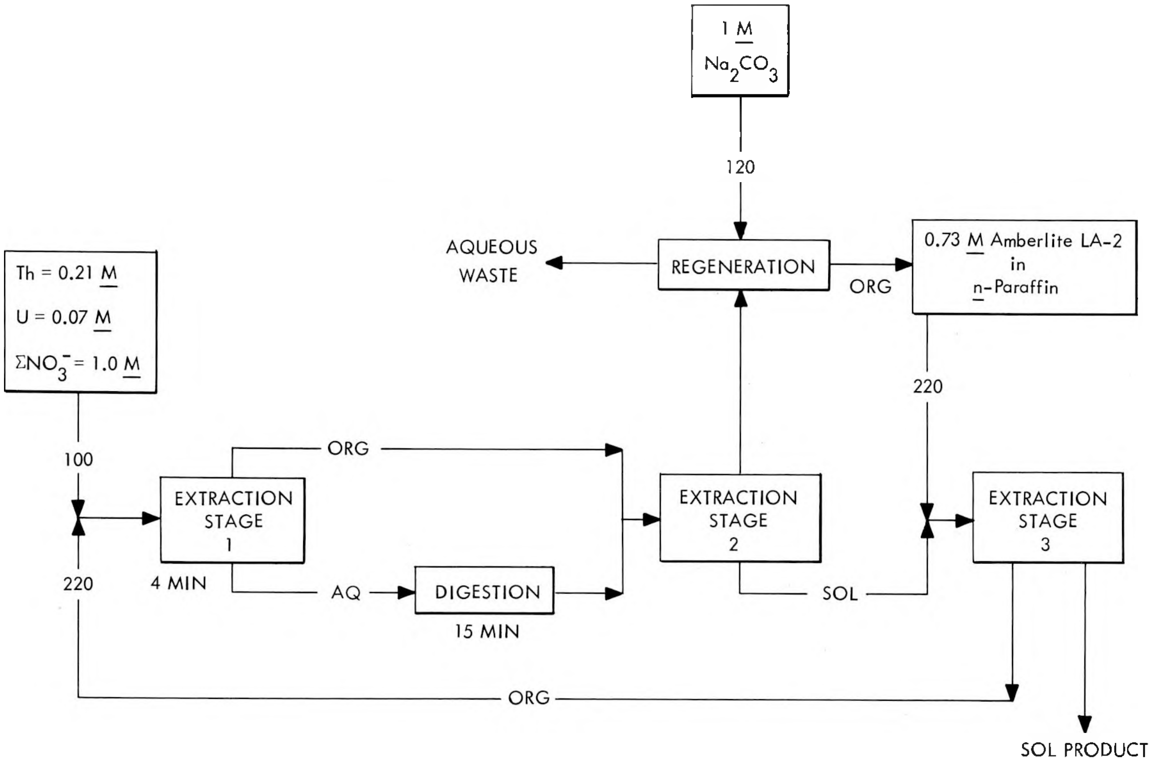

Fig. 2. Flowsheet for Engineering Studies of Amine Denitration Process.

limit of error for a single nitrate value was ± 26% for the Kjeldahl method and ± 28% for the colorimetric method. Since most of the nitrate values in this report are the average of at least two determinations for the same or parallel sols, their limit of error at the 95% confidence level is a maximum of about ± 20%. The pH decreased over the two-month period, indicating a release of acid.

The procedures used in preparing the sols described in this report will be denoted by an expression of the form BXC • YD • XC. The expression signifies that, first, the aqeuous solution was heated to boiling (B), or in some cases to a lower specified temperature, and the hot aqueous contacted (C) for X minutes with the extractant which was at room temperature. Then phases were allowed to separate, and the aqueous phase was digested (D) for Y minutes at reflux, or at some lower specified, temperature. After the digestion, the hot aqueous was immediately contacted again (C) for X minutes with extractant. If more than two contacts and/or digestion periods are used, they will be given in a similar manner. The organic flow will be given as crosscurrent (in which fresh amine solution is used in each contact), countercurrent (in which fresh amine solution is used in the last stage initially, then in the preceding stages), or cocurrent (in which fresh amine solution is used in the first stage and is subsequently reused in each succeeding extraction stage).

3.1 Extraction Time and Temperature

The nitrate extraction equilibrium, like other amine extraction equilibria,[12,13] is achieved very rapidly, and 1 minute of thorough mixing is sufficient for the extraction of all the extractable nitrate from thorium-uranyl nitrate solutions. This was confirmed by tests that are summarized in Table 1. The sols were prepared from solutions that were about 0.19 M in thorium nitrate and 0.06 M in uranyl nitrate. The procedure used was BXC • 10D • XC, with X being varied from 1 to 10 min. About 1.5 moles of amine (0.75 M Amberlite LA-2 in n-dodecane) per mole of initial nitrate were used cocurrently in the extraction steps. The nitrate:metal mole ratio achieved in all the sols was about 0.20, with pH values ranging from 4.05 to 4.18. (A slightly lower value, 0.16, was obtained for several preparations made using a 30-min contact period and smaller amine:nitrate mole ratios to denitrate aqueous thorium solutions containing about 22 mole % uranium.) As would be expected, the nitrate:metal mole ratio remained unchanged, regardless of the contact times used in the first and second extractions; for example, a procedure of B5C • 10D • 10C also produced a sol with a final nitrate:metal mole ratio of 0.20. While these results indicate that a 1-min extraction period should be sufficient, a minimum of 2 min was used in the subsequent tests to compensate for possible mixing variations.

Small quantities of uranyl and thorium nitrate are extracted by the amine. The effects of extraction time, temperature, amine concentration, and total metal concentrations of the feed on these losses were investigated; some trends were found (Appendix, 9.1). However, preliminary large-scale runs indicated that losses from entrainment will be much higher than those resulting from extraction, and will necessitate a recovery system.[10] The latter will consist of a very dilute acid or water scrub of the amine just prior to the regeneration step. The aqueous scrub will then be returned to the first extraction stage for recycle.

Table 1. Effect of Extraction[a] Time on Nitrate:Metal Mole Ratio

Extraction time, min	1	2	5	10
Nitrate:metal ratio	0.22	0.20	0.20	0.23
pH	4.05	4.05	4.05	4.18

[a] Conditions:

Procedure: BXC · 10D · XC, where X = 1 to 10 min.
Amine phase: 0.75 Amberlite LA-2 in n-dodecane
Amine flow: Cocurrent
Feed: $Th(NO_3)_4$, ~0.19 M
$UO_2(NO_3)_2$, ~0.063 M
Amine:initial nitrate mole ratio: ~1.5

Phase separation time after extraction was on the order of 1 to 2 min in most laboratory-scale preparations; slightly faster separations were obtained at higher temperatures (30 to 60°C) than at room temperature.

3.2 Organic Flow Patterns and Mixing Technique

The nitrate:metal ratio in the sol appears to be independent of the flow pattern used in the extraction stages. For example, in the preparation of a thorium-uranium sol containing 22 to 25 mole % uranium, the final nitrate:metal mole ratio was about 0.20 with cocurrent, countercurrent, or crosscurrent flow of the amine in the extraction stages (Table 2). These sols were prepared, using 1.2 moles of amine per initial mole of nitrate, with extraction periods of at least 2 min and a 10-min digestion period. The cocurrent flow offers the possible advantage of decreasing the uranium extraction losses (if the entrainment losses could be reduced to a similar or lower level), since it allows the uranium that is extracted in the first stage to reestablish equilibrium at lower aqueous nitrate concentrations in succeeding stages.

Table 2. Effect of Type of Flow of Amine on Nitrate:Metal Mole Ratio

Amine:nitrate mole ratio = 1.2

Type of Flow	Nitrate:Metal Mole Ratio	pH
Countercurrent	0.19	4.94
Cocurrent	0.20	4.40
Crosscurrent	0.21	4.76
Average value	0.20	4.70

It is imperative that the extraction stages be run with the organic phase continuous in order to ensure good phase separation. In most experiments in which the method was used, phase separation occurred in 1 to 2 min or less. However, if the aqueous was the continuous phase, especially in the first extraction stage, emulsions formed that were difficult, in fact often impossible, to break. A small amount of interfacial emulsion is formed in the first stage even with the organic phase continuous. In the laboratory tests the volume of this emulsion was estimated to be a maximum of 1.5 to 2% of the feed volume; however, it was reduced to about 0.1% or less after the second extraction. In experiments using cocurrent flow, this emulsion was usually allowed to be carried with the organic phase after the first contact; however, the same volume reduction was observed, regardless of whether the emulsion was carried with the aqueous or the organic phase into the second extraction stage.

3.3 Type of Amine

Sols were prepared, using such amines as Adogen 364, Ditridecyl P, Amberlite LA-2, 1-nonyldecyl amine, and Primene JM-T. Most of the laboratory studies were made with Amberlite LA-2, an extensively branched secondary amine (N-lauryl trialkylmethyl amine). It is an effective, commercially available nitrate extractant and does not require any additives in the diluent.

The ability of the aforementioned amines to extract nitrate was measured, using n-dodecane solutions of the compounds to extract the nitrate from an aqueous solution that was about 0.22 M in thorium nitrate and 0.004 M in uranyl nitrate. A B2C · 10D · 2C · 10D · 2C procedure and amine:nitrate mole ratios of 1.2 or 1.4 were used, except in the case of Primene JM-T. A ratio of only 0.8 was used for the latter amine because higher ratios caused precipitation in the first extraction stage. Since this amine is appreciably more basic than the secondary and tertiary amines, it would be expected to extract more nitrate and thus possibly cause precipitation. Crosscurrent flow was used; therefore, a large excess of amine was present in the second and third extraction stages; however, this had no apparent adverse effect. Only the extractable nitrate formed during digestion was extracted. The extra digestion and extraction stage was used merely to ensure that the nitrate extraction was complete. The nitrate:metal ratios in the final sols were 0.14 to 0.17 (Table 3) with each of the amines except Adogen 364. A ratio of 0.24 was obtained in the latter case, but this value may be high because of analytical uncertainties. Addition of 10 vol % tridecyl alcohol to the diluent for this amine was necessary in order to prevent the formation of a second organic phase during the extraction cycle.

Table 3. Preparation[a] of Mixed Thorium-Uranium Oxide Sols with Various Amines

Type of Amine	Amine[b]	Concentration (M)	Amine:Initial Nitrate Mole Ratio	Nitrate:Metal Mole Ratio of Sol	pH of Sol
Tertiary	Adogen 364[c]	0.5	1.2	0.24	5.30
Secondary	Ditridecyl P	0.5	1.2	0.15	6.05
	Amberlite LA-2	0.75	1.2	0.17	5.42
Primary	n-nonyldecyl	0.2	1.4	0.14	6.32
	Primene JM-T	0.5	0.8	0.17	6.23

[a] Conditions:

Procedure: B2C · 10D · 2C · 10D · 2C
Flow: Crosscurrent except in case of Amberlite LA-2, which was countercurrent
Aqueous Feed: 0.26 M thorium nitrate plus uranyl nitrate
Final sol contained 17 mole % uranium

[b] Amines:

Adogen 364 = tri-n-alkylamine (average C_9)
Ditridecyl P = mixture of alkyls from tetrapropylene containing a total of 13 carbon atoms
Amberlite LA-2 = N-lauryl trialkylmethyl amine
Primene JM-T = trialkylmethylamine

[c] Diluent is n-dodecane + 10 vol % tridecyl alcohol; all others are n-dodecane

3.4 Amine:Nitrate Mole Ratio

Excess amine (i.e., more than the stoichiometric amount as indicated by the amine:nitrate mole ratio of 1.2 to 1.5) is needed to ensure sufficient nitrate extraction. Thorium oxide--uranium oxide sols containing from 22 to 25 mole % uranium were prepared, using 0.8 to 3 moles of amine per mole of initial nitrate in the extraction stages. The B ≥ 2C • 10D • ≥ 2C procedure was used with 0.6 to 0.78 *M* Amberlite LA-2 in *n*-dodecane. With the exception of the experiment using 0.8 mole (which was not sufficient amine to remove all the extractable nitrate), all the sols had final nitrate:metal mole ratios of about 0.2, ranging from 0.17 to 0.24 (Table 4).

Table 4. Effect of Amine:Nitrate Mole Ratio on the Nitrate:Metal Mole Ratio

Amine:initial nitrate mole ratio	0.8	0.95	1.1	1.2	1.25	1.5	2.0	3.0
Nitrate:metal mole ratio	0.57	0.17	0.24	0.20	0.20	0.19	0.20	0.17
pH	3.22	4.22	4.50	4.70	4.19	4.05	4.40	4.72

3.5 Amine Concentration

The nitrate-to-metal ratio was found to be independent of the amine concentration in a series of sols prepared with 0.30 to 1.0 *M* Amberlite LA-2 in *n*-dodecane. The value was approximately 0.20 for each preparation (Table 5). Most of the laboratory experiments were made with either 0.6 or 0.75 *M* amine since the 1 *M* test exhibited a slightly slower phase separation than the more dilute organics.

3.6 Diluent

The values of the nitrate-to-metal ratios of sols that were prepared with Amberlite LA-2 in various diluents differed only slightly. The ratios ranged from 0.26 for benzene to 0.20 for Amsco 125-82 or *n*-paraffin (Table 6). These values are within the limits of analytical accuracy. Although all the extractions were made with the organic as the continuous phase, some of the diluents separated slightly faster and formed fewer interfacial emulsions than others. The most efficient diluents in these tests were *n*-dodecane, or its commercial equivalent *n*-paraffin, and diisopropylbenzene. The first two were chosen for laboratory and scaleup studies because of availability and ease of handling.

Table 5. Effect of Amberlite LA-2 Concentration on Nitrate:Metal Mole Ratio of Sol[a]

Concentration, *M*	1	0.75	0.60	0.30
Nitrate:metal mole ratio	0.22	0.19	0.22	0.20
pH	5.00	4.25	4.35	4.40

[a] Conditions:

Diluent: *n*-dodecane
Procedure: B(5 to 6)C · (10 to 20)D · (5 to 6)C
Amine:nitrate mole ratio: 1.2 to 1.5
Feed: $Th(NO_3)_4$ = 0.19 to 0.27 *M*
$UO_2(NO_3)_2$ = 0.06 to 0.09 *M*
Sol: mole % U = 25

Table 6. Effect of Diluent on Nitrate:Metal Mole Ratio of Sol[a]

Diluent	Nitrate:Metal Mole Ratio of Sol	pH of Sol
Benzene	0.26	4.68
Diethylbenzene	0.22	5.04
Diisopropylbenzene	0.24	4.10
Amsco 125-82	0.20	4.70
n-dodecane	0.21	4.35
n-paraffin	0.20	4.05

[a] Conditions:

Amine: 0.6 to 0.75 *M* Amberlite LA-2
Procedure: B5C · 10$\overline{D}$ · 5C
Amine:nitrate mole ratio: 1.2 to 1.5
Feed: $Th(NO_3)_4$ = 0.19 to 0.28 *M*
$UO_2(NO_3)_2$ = 0.06 to 0.09 *M*

3.7 Aqueous Metal Concentration

A series of sols, containing 25 mole % uranium, that were prepared with different metal concentrations in the aqueous feeds showed that the total metal concentration must be less than 0.6 M to prevent the formation of solids during the extraction step (Table 7). Although these solids will liquefy on heating, they could cause difficulties in a continuous process. The values presented in Table 7 are the averages for several sols that were prepared using about 1.2 to 1.5 moles of Amberlite LA-2 per mole of initial nitrate. The diluent was either n-dodecane (or its commercial equivalent n-paraffin), and the extraction periods were 2 to 30 min with a 10- to 30-min digestion period between. The sol with the lowest metal concentration (0.085 M) had a slightly higher nitrate:metal mole ratio (0.21) than that of the others (average value, 0.16); this is probably the result of analytical uncertainty. If other thorium-uranium mole ratios were used, the maximum feed concentration would probably be about the same as that above but would need to be determined accurately before use in plant operation.

Table 7. Effect of Total Metal Concentration on Nitrate:Metal Mole Ratio of Sol

Concentration (M)		Nitrate:Metal	
Thorium	Uranium	Mole Ratio of Sol	pH of Sol
0.063	0.022	0.21	4.58
0.125	0.044	0.17	4.87
0.249	0.085	0.15	5.07
0.30	0.10	0.16	5.10
0.38	0.13	0.16	4.95
0.45	0.15	Gelled during first extraction	
0.52	0.18	Gelled during first extraction	

3.8 Digestion

It is necessary to heat the aqueous phase after removing the initially extractable nitrate in order to form a sol and to release more nitrate, which can be removed in the second extraction step. Usually one such digestion is sufficient. For example, an aqueous solution 0.2 M in $Th(NO_3)_4$ was contacted seven times (contact time, 5 min) with 1.7 moles of 0.75 M Amberlite LA-2 (in n-dodecane) per mole of initial nitrate. After the first contact, the nitrate:metal mole ratio was 0.8, and it remained at this value after the six remaining contacts with amine. This experiment was repeated except that the aqueous phase was digested for 10 min at ≥98°C after each extraction. In this case the nitrate:metal mole ratio decreased to about 0.3 after the second contact and did not change with further digestions and contacts with the amine.

For the optimum effect, the partially denitrated aqueous phase must be digested for at least 8 to 10 min at ≥98° (reflux temperature = ~100°C). Shorter digestion periods give nitrate:metal ratios of about 0.3, compared with about 0.17 for 10-min to 24-hr digestion periods (Table 8). These ratios appear to decrease at the longer digestion time; however, the reported values are within the limit of analytical accuracy (± 20%). The ratios shown in Table 8 were obtained for sols that were prepared by using an amine:initial nitrate mole ratio of 1.2 in the extractions. The organic phase consisted of 0.6 to 0.75 M Amberlite LA-2 in n-dodecane (or n-paraffin) and was contacted for 5 to 10 min with the aqueous phase before and after the specified digestion time. The aqueous phase was 0.19 M in thorium nitrate and 0.06 M in uranyl nitrate. In the first extraction the aqueous phase was heated to boiling and then immediately contacted with the organic phase.

Table 8. Effect of Digestion Time on Nitrate:Metal Mole Ratio

Digestion[a] Time (min)	Properties of Sol After Second Contact	
	Nitrate:Metal Ratio	pH
4	0.35	4.80
6	0.32	4.69
8	0.26	4.59
10	0.19	3.89
12	0.21	4.01
15	0.18	4.36
20	0.18	4.51
30	0.17	4.10
60	0.18	4.75
180	0.16	4.98
360	0.15	4.50
960	0.16	4.64
1440	0.14	4.96

[a] Digestion was at a temperature of ≥98°C.

To ensure a reasonably short digestion time, the temperature of the aqueous phase must be maintained at 95 to 100°C. Sols were prepared by using a B6C • 20D • 6C • 20D • 6C procedure with digestion temperatures of 80, 90, 95°C, and the reflux temperature of ~100°C. The nitrate:metal mole ratio was measured after each extraction (Table 9). Results showed that at the lower digestion temperatures (80 and 90°C) nitrate was removed in the third extraction, whereas at the higher temperatures equilibrium was achieved after two extractions. Thus, longer digestion periods may be necessary at the lower temperatures.

Table 9. Effect of Digestion Temperature on Nitrate:Metal Mole Ratio of Sol[a]

Digestion Temperature (°C)	Nitrate:Metal Mole Ratio After		
	First Contact	Second Contact	Third Contact
80	0.45	0.38	0.37
90	0.46	0.33	0.23
95	0.45	0.18	0.17
101	0.48	0.19	0.17

[a] Conditions:

Procedure: B6C · 20D · 6C · 20D · 6C
Amine: 0.75 M Amberlite in n-paraffin
Amine:nitrate mole ratio: 1.5
Flow: Cocurrent
Aqueous: 0.22 M $Th(NO_3)_4$ + 0.07 M $UO_2(NO_3)_2$

3.9 Thorium-Uranium Ratio

Stable thorium-uranium sols containing 0 to 68 mole % uranium (Table 10) were prepared from aqueous solutions that were 0.22 to 0.30 M in thorium nitrate--uranyl nitrate by extracting the nitrate with 0.77 M Amberlite LA-2 in n-paraffin. An amine:initial nitrate mole ratio of 1.5, and cocurrent flow were used. A multiple contact procedure, B6C · 20D · 6C · 20D · 6C · 20D · 6C, was used to ensure that equilibrium of the nitrate had been attained in the final sols. From 98 to 99.6% of the extractable nitrate (93 to ~95% of the total aqueous nitrate; see Table 10) was extracted in the first two extraction stages.

Table 10. Preparation[a] of Thorium-Uranium Sols

	First Extraction		Second Extraction		Third Extraction		Fourth Extraction	
Mole % U	Nitrate:Metal Mole Ratio	pH	Nitrate:Metal Mole Ratio	pH	Nitrate:Metal Mole Ratio	pH	Nitrate:Metal Mole Ratio	pH
0	0.73	4.46	0.31	4.33	0.28	4.99	0.28	4.31
2.5	0.68	4.24	0.30	3.93	0.28	4.74	0.26	4.47
5.3	0.67	5.00	0.28	4.09	0.24	4.57	0.25	4.65
9.4	0.62	4.71	0.25	4.61	0.24	4.84	0.23	4.88
18	0.55	4.84	0.21	5.02	0.20	4.38	0.19	4.46
26	0.45	4.13	0.19	4.27	0.16	4.46	0.16	4.50
35	0.39	4.76	0.23	4.67	0.19	4.67	0.16	4.77
53	0.26	4.92	0.20	5.12	0.20	5.14	0.18	5.06
68	0.25	5.06	0.16	5.46	Gelled	-	-	-

[a] Conditions:

Procedure: B6C · 20D · 6C · 20D · 6C · 20D · 6C
Amine: 0.77 M Amberlite LA-2 in n-paraffin
Amine:nitrate mole ratio: 1.5
Flow: cocurrent
Aqueous concentration: 0.22 to 0.30 M thorium plus uranium

The nitrate:metal mole ratio of the sol after the first extraction stage decreased linearly as the amount of uranium increased from 0 to about 50 mole % uranium. From 50 to 68 mole % uranium, the ratio remained constant at about 0.25. The ratio at equilibrium also decreased linearly from 0 to about 25 mole % uranium and then remained constant at about 0.16 mole of nitrate per mole of total metal (Fig. 3).

The sol containing 68 mole % uranium formed a gel during the third extraction. Attempts to prepare a uranium sol directly from uranyl nitrate solutions by denitration with Amberlite LA-2 were unsuccessful. The nitrate:metal ratio would reach about 1 and then remain constant during any further denitration.

4. EVAPORATION STUDIES

Sols were evaporated to concentrations of about 1.2 to 4.3 M in total metal before being used to form microspheres. The maximum obtainable concentrations appeared to be strongly influenced by the nitrate content of the sols. Table 11 shows data for several sols (having different nitrate:metal ratios) that were inadvertently concentrated to gelation and then resuspended by dilution. Although these data are not conclusive from the standpoint of maximum concentrations that can be obtained before gelation, they may serve as guidelines for future evaporations. For example, sols with nitrate:metal ratios of about 0.1 or less will probably remain liquid up to a total metal concentration of about 1.5 M, whereas those with a ratio of about 0.15 may be concentrated until they are 2 M in total metal. Sols with the higher ratios, 0.2 to 0.25, could probably be concentrated to about 4 M in total metal before gelation would occur.

X-ray measurements of the crystallite size of a number of concentrated sols were made (Table 12). The average value obtained was 36 to 40 A; however, an electron micrograph showed particles as small as 10 A (Fig. 4). These values should be contrasted with those usually obtained (60 to 70 A) for the thorium-uranium sols that were prepared from steam-denitrated thoria in the original sol-gel process.

Attempts were made to grow larger particles by seeding the aqueous phase, either during the first extraction or the digestion stage, with up to 20 vol % of a previously prepared sol. There was no change in the final nitrate:metal ratio and slight, if any, increase in crystallite size (see Table 12).

The first sols prepared in the pilot-plant equipment were opaque dark-orange sols and had crystallite sizes in the (111), (220), and (311) planes of 58 ± 2, 47 ± 3, and 43 ± 2 A respectively (Table 12). While these values are greater than those obtained for the transparent clear-red sols prepared in the laboratory, the difference in size is not enough to account for the difference in physical appearance; this would require a crystallite size two to three times that of the laboratory sols.[14]

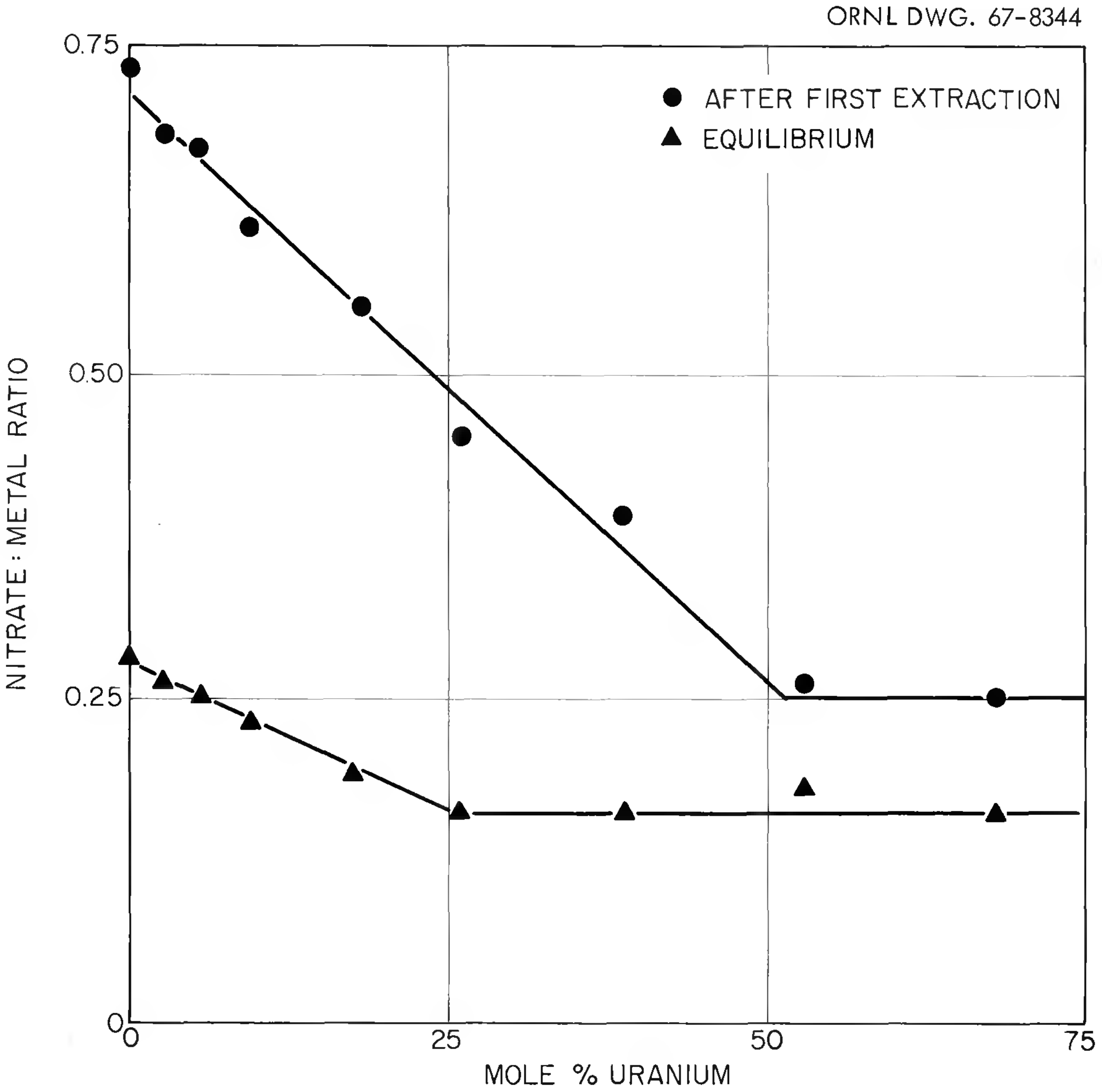

Fig. 3. Nitrate:Metal Ratio as a Function of Mole % Uranium.

Table 11. Concentrated Sols of Different Nitrate:Metal Ratios

Nitrate:Metal Mole Ratio	Thorium:Uranium Mole Ratio	Total Metal Concentration (M)[a] "Liquid"	Total Metal Concentration (M)[a] Gel	Evaporation Conditions Pressure (mm Hg)	Evaporation Conditions Max. Temp. (°C)
0.06	3.00	1.56	-	100	56
0.11	3.42	1.15	1.70	100	42
0.14	2.88	1.94	-	100	74
0.16	2.92	1.96	2.26	100	70
0.19	3.78	1.42	b	Atmospheric	140
0.20	3.01	2.54	-	100	34
0.21	3.01	4.32	Gelled after 1 week	100	45
0.25	3.64	3.57	4.3	100	61

[a] The values for "liquid" and gel are only those observed and do not represent either the maximum concentration to maintain a liquid state or the minimum for gelation.

[b] At 1.72 M this sol remained liquid for several days before thickening.

Table 12. Crystallite Sizes as Determined by X-Ray Measurements

Crystallographic Orientation	Average Crystallite Size[a] (A) Laboratory Sols	Seeded Sols	Pilot-Plant Sols
(111)	40 ± 2	46 ± 5	58 ± 2
(220)	37 ± 1	41 ± 5	47 ± 3
(311)	36 ± 1	39 ± 4	43 ± 2

[a] Deviations are for 95% confidence level.

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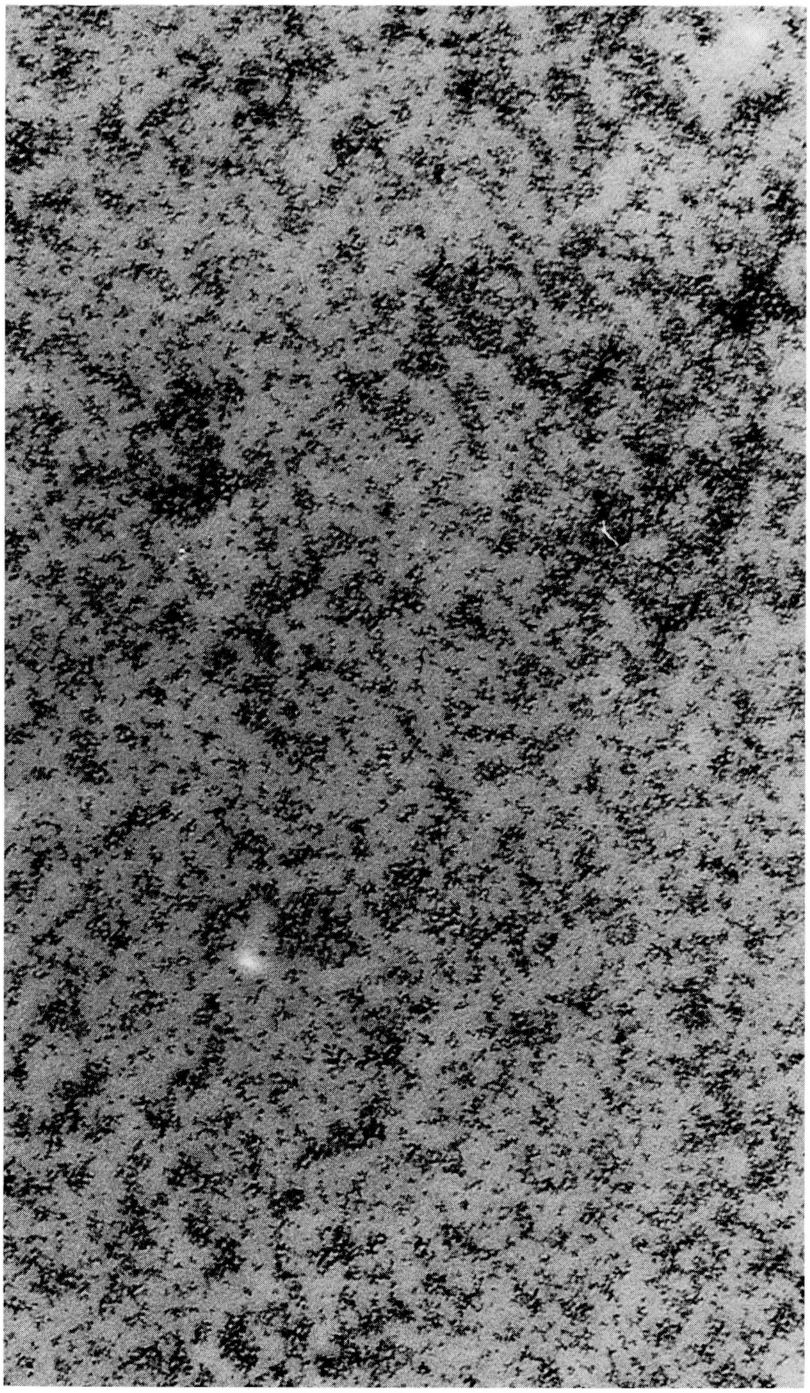


Fig. 4. Electron Micrograph of Sol Prepared by Amine Denitration Process (1 mm = 53 A).

5. MICROSPHERE PREPARATION

The investigation of the conditions suitable for forming microspheres from these sols has been of a semiquanitative, and often cursory, nature. However, the studies showed that excellent microspheres can be formed from sols that are made by the Amine Denitration Process. The dilute sols are evaporated until they are 1 to 2 M in total metal content; then spheres are formed by injecting these concentrates into a dehydrating medium such as 2-ethyl-1-hexanol containing suitable surfactants to prevent the droplets from coalescing or clustering. These sols were found to be more sensitive to the type and concentration of surfactant than mixed sols formed by other methods. For example, in the formation of microspheres from a sol prepared by blending thoria and urania sols in a 3.5:1 ratio, we used 2-ethyl-1-hexanol that contained 0.3 vol % Span 80 (sorbitan monooleate) and 0.5 vol % Ethomeen S-15 (the condensation product of a primary fatty amine with ethylene oxide).[15] These same column conditions would cause severe cracking and/or "cherry pitting" of microspheres formed from a sol prepared by using the amine process. Satisfactory spheres have been made from the latter type of sol, using these two surfactants; however, the concentrations of each was reduced to about 0.1 vol % or less. Excellent spheres were made from some of the first sols made in the pilot-plant equipment by reducing the surfactant concentrations to 0.04 vol % of each and increasing the water content of the 2-ethyl-1-hexanol to 1.5 or 1.8 vol % to decrease the rate of drying.

Some evidence obtained in these studies showed that the surfactant sensitivity of the sols was dependent on the temperature used during and/or after evaporation. In view of this, the results to be presented below are definitive only for the particular sol that was used; however, they should be pertinent to future work, in that they can serve as guidelines in the determination of conditions for forming microspheres.

Sols that were evaporated under vacuum at 30 to 38°C were much more sensitive to column conditions and thus more difficult to form into spheres than sols that had been evaporated slowly at atmospheric pressure and reflux temperatures (~100°C). Sols that were concentrated at the lower temperatures became amenable to sphere formation if digested at an elevated temperature after the evaporation. A sol that was 1.10 M in thorium, 0.32 M in uranium, and 0.30 M in nitrate was concentrated by evaporation at reflux temperatures and atmospheric pressure. It formed excellent microspheres with the use of 2-ethyl-1-hexanol containing 0.5 vol % H_2O and 0.8 vol % of the surfactant Alkanol OE. These same conditions produced only fragments with a sol that had been evaporated at 100 mm Hg pressure at a temperature of 33 to 38°C. This concentrated sol was 1.97 M in thorium, 0.68 M in uranium, and 0.49 M in nitrate. Decreasing the Alkanol content to 0.2 vol % made only a slight improvement in the spheres that were formed; however, refluxing the sol for 30 min prior to forming the spheres caused a marked improvement. Still further improvement was observed when the drying rate was decreased by increasing the water content of the 2-ethyl-1-hexanol from 0.5 to 1 vol %.

Table 13 shows the effect of digestion (of the concentrated sol) on the sphere-forming capability. Aliquots of the thorium:uranium sols (atom ratio, 3:1) described above were digested 30 min at 70 to 80°C and 30 min at reflux temperatures. Spheres were then made from these three sols by injecting small amounts of each into 2-ethyl-1-hexanol containing 1 vol % H_2O and equal concentrations of Span 80 and Ethomeen S-15 ranging from 0.04 to 0.15 vol %. The percentage yield of good spheres vs surfactant concentration was used as a measure of sensitivity. In each case the spheres remained in the dehydrating medium for 30 min and were dried overnight at 70 to 80°C and then 5 hr at 180°C. Previous data had indicated that if microspheres survived this drying treatment they would usually survive the calcining treatment. Results showed that the order of sensitivity was as follows: undigested sol > the 70 to 80°C digested material > the refluxed concentrate. For example, it required only 0.08 vol % of each of the surfactants to reduce the yield from the undigested sol to 50%; on the other hand, 0.15 vol % was required for the same effect on the sol that had been digested at 70 to 80°C, whereas at 0.15 vol % the yield was 90% for the refluxed material. (We do not know why the yield from the undigested sol increased to about 60% at the 0.15 vol % concentration level.) Caution must be used in digesting the concentrated sols. A sol that was concentrated until it was about 1.54 $\underline{M}$ in thorium, 0.51 $\underline{M}$ in uranium, and 0.335 $\underline{M}$ in nitrate gelled completely after digesting 3.5 hr at 75 to 90°C. This sol had been a stable liquid for 2 days prior to digestion.

A semiquantitative study of a number of surfactants was made in an effort to find possible substitutes for Span 80 and Ethomeen S-15. Two of the more promising compounds were Alkanol OE, a long-chain alcohol--ethylene oxide condensation product, and bis(2-ethoxyethyl)phthalate. Spheres were formed by injecting a sol (1.10 $\underline{M}$ in thorium, 0.32 $\underline{M}$ in uranium, 0.30 $\underline{M}$ in nitrate, and 0.01 $\underline{M}$ in carbon of an unspecified form) into 2-ethyl-1-hexanol containing 0.5 vol % H_2O and various concentrations of the surfactant in question. The compounds were used alone and in mixtures as additives both to the dehydrating medium and, in a few cases, to the sol. After 30 min the spheres were removed from the column; they were dried overnight and then heated to 170 to 180°C for 5 to 6 hr. Gram-sized batches were prepared with some of the more promising compounds. In these tests the perfect spheres were separated and weighed to determine the percentage yield. Results of all these studies are shown in Tables 14-17.

Alkanol OE may serve as a substitute for both Span 80 and Ethomeen S-15. A concentration of about 0.2 vol % prevented both clustering and coalescing of the spheres. The concentration did not appear to be critical, since it could be increased to 0.8 vol % without adverse effects. At the lower concentration, Alkanol OA, a similar compound but with a shorter ethylene oxide chain, had no effect on coalescing but prevented clustering; however, at 0.8 vol % it produced sphere deformation. Another similar compound, but with a longer ethylene oxide chain, Alkanol OJ, produced fair spheres at concentrations of 0.1 to 0.2 vol %; however, at higher concentrations, it caused cracking and deformation (Table 14).

Table 13. Effect of Digestion of Concentrated Sol on Sphere Formation

Surfactant Concentration[a] (vol %)		Percentage Yield[b]		
Span 80	Ethomeen S-15	Undigested Sol	Sol Digested at 70 to 80°C	Sol Digested at 100°C
0.04	0.04	97	90	97
0.06	0.06	85	85	90
0.08	0.08	50	90	98
0.10	0.10	25	90	95
0.15	0.15	60	50	90

[a] Dehydrating medium: 2-ethyl-1-hexanol containing 1 vol % H_2O.

[b] All yields are approximations.

In the preparation of gram quantities of spheres, 92 to 95% of the spheres were satisfactory in 2-g batches that were formed in 2-ethyl-1-hexanol containing 0.5 vol % H_2O and 0.4 to 0.8 vol % Alkanol OE. About 72% of a 2.2-g batch made by using 0.1 vol % Alkanol OJ was good, as was 88% of a 2.4-g batch prepared with Alkanol HC, another member of this surfactant family (Table 17).

The Gafco-Emulphogenes and the Hodags were not examined as carefully as the Alkanols; however, they are also possible substitutes for Span 80 and Ethomeen S-15. Small amounts (0.05 to 0.1 vol %) prevented both coalescing and clustering (Table 14).

Another promising surfactant is bis(2-ethoxyethyl) phthalate. Although it does not affect coalescing, 0.6 to 1.2 vol % in the dehydrating medium is quite effective in preventing clustering. A 2-g batch of spheres was formed using 2-ethyl-1-hexanol containing 0.6 vol % bis(2-ethoxyethyl) phthalate to prevent clustering and 0.04 vol % Ethomeen S-15 to prevent coalescing. More than 93% of these spheres were satisfactory; however, on increasing the concentration of the surfactants to 0.75 and 0.08 vol %, respectively, the yield decreased to 78%. This decrease was due primarily to the increased concentration of the Ethomeen S-15.

Several surfactants were incorporated directly in the sol prior to sphere formation. Both Ethomeen S-15 and Igepal CO 990 prevented coalescing; when used in combination they prevented clustering and coalescing but caused extensive sphere breakage (Table 15). A 1.1-g batch of spheres was formed using 0.01 vol % Ethomeen S-15 in the sol (to prevent coalescing) and a dehydrating medium containing 0.8 vol

Table 14. Effects of Surfactants in Dehydrating Medium on Sphere Formation

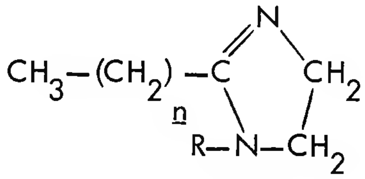
Surfactant	Class or Formula	Concentration Range (vol %)	Remarks
Amine O	Heterocyclic tertiary amine derived from oleic acid 	0.1-0.2	Prevents clustering; however, 0.1 vol % causes some cracking and 0.2 vol % produces cherry pits.
Ethomeen S-15	Condensation product of primary fatty amine with ethylene oxide	0.01-0.5	Prevents coalescing; at 0.1 vol % some cracking occurs; some cherry pits appear at 0.2 vol %; all spheres contain cherry pits at 0.3 vol %. The spheres were completely shattered at 0.5 vol %.
Span 80	Sorbitan monooleate	0.01-0.1	Prevents clustering; however, 0.1 vol % produces flaws and splinters.
Triton X-45	Isooctyl phenyl polyethoxyethanol OPE-5	0.01-0.12	Little effect on clustering or coalescing; at 0.12 vol %, cherry pits appear.
Paraplex G-62	Condensation product of soybean oil and ethylene oxide	0.05-0.6	Prevents clustering completely at 0.4 vol % but does not affect coalescing.

Table 14 (continued)

Surfactant	Class or Formula	Concentration Range (vol %)	Remarks
Bis(2-ethoxyethyl) phthalate	1,2-$C_6H_4(COOCH_2CH_2OC_2H_5)_2$	0.1-1.5	Prevents clustering at about 0.6 vol % or greater; however, does not affect coalescing. More than 1.2 vol % causes some breakage and deformation of the spheres.
Butyl Carbitol	$CH_3(CH_2)_3OCH_2CH_2OCH_2CH_2OH$	0.1-1.0	Slight effect on clustering at 1 vol %; no effect on coalescing.
Amberlite LA-2	N-Lauryl trialkylmethyl amine	0.04-0.2	Does not affect clustering or coalescing; 0.2 vol % produces cherry pits.
Alkanol OA	Long-chain-alcohol--ethylene oxide condensate $R(OCH_2CH_2)_{\underline{n}}OH$	0.02-0.8	No effect on coalescing but prevents clustering above 0.1 vol %; at 0.8 vol %, some spheres cracked and cherry pitted.
Alkanol OE	Similar to Alkanol OA but $\underline{n}$ is larger	0.02-0.8	Prevents clustering at 0.1 vol %; prevents coalescing at 0.2 vol %; no adverse effects up to 0.8 vol %.
Alkanol OJ	Similar to Alkanol OE but $\underline{n}$ is larger	0.02-0.5	Prevents coalescing at 0.02 vol %; prevents clustering at 0.1 vol %. Spheres begin breaking at 0.2 vol %; cherry pitting and deformation at 0.5 vol %.
"Alfol 12"	Long-chain alcohol	0.02-0.5	No effect on clustering or coalescing.

Table 14 (continued)

Surfactant	Class or Formula	Concentration Range (vol %)	Remarks
<u>Mixtures</u>	See above		
Bis(2-ethoxyethyl) phthalate plus Ethomeen S-15		0.6-0.75 0.04-0.16	No coalescing or clustering; however, at 0.08 vol % Ethomeen S-15, some sphere breakage occurs; at 0.16 vol % Ethomeen, all spheres have cherry pits.
Paraplex G-62 plus Ethomeen S-15	See above	0.6 0.03-0.1	No coalescing or clustering; however, some breakage occurs at 0.1 vol % Ethomeen.
Butyl carbitol plus Ethomeen S-15	See above	1.0 0.04	Prevented coalescing and most clustering.
Hodag 62-0	Polyoxyethylene glycol (600) dioleate	0.02-0.2	Prevents coalescing and clustering above 0.05 vol %; at 0.2%, cherry pits appear.
Hodag 152-0	Polyoxyethylene glycol (1500) dioleate	0.05-0.8	Required about 0.2 vol % for good spheres; at 0.4 vol %, cherry pits appear.
Marchon BQ100	Polyethylene glycol (400) monooleate	0.02-0.8	No coalescing at 0.2 vol %; clustering stopped at 0.5 vol %; few cracked spheres noted at 0.9 vol %.

Table 14 (continued)

Surfactant	Class or Formula	Concentration Range (vol %)	Remarks
Gafco-Emulphogene BC-420	Tridecyloxypoly(ethyleneoxy)ethanol	0.02-0.6	No coalescing or clustering above 0.1 vol %, some cherry pitting occurs at 0.6 vol %.
Gafco-Emulphogene BC-720	As above	0.02-0.4	No coalescing or clustering above 0.05 vol %; cherry pits occur above 0.2 vol %.
Gafco-Emulphogene BC-610	As above	0.02-0.4	No coalescing or clustering at 0.05 vol %; at higher concentrations, cherry pits appeared and spheres stuck to walls.

Table 15. Effects of Surfactants in Sol on Sphere Formation

Surfactant	Class or Formula	Concentration Range (vol %)	Remarks
Ethomeen S-15	See Table 14	0.001-2	Prevents coalescing at 0.01 vol % and reduces clustering above 0.1 vol %; sol becomes viscous at 1% and a gel at 2%.
Tritox X-45	See Table 14	0.002-2	No effect.
Paraplex G-62	See Table 14	0.002-2	Little, if any, effect.
Span 80	See Table 14	0.001-2	0.2 vol % decreases clustering slightly; higher concentrations from precipitation.
Igepal CO 990	Nonylphenoxypoly-(ethyleneoxy) ethanol	0.002-0.2	Prevents coalescing at 0.002 vol % but causes some sphere breakage at 0.2 vol %.
Igepal CO 990 plus Ethomeen S-15	See Table 14 and above	0.01 0.01	Less clustering and no coalescing, but much breakage.
Ethomeen S-15 plus Paraplex G-62	See Table 14	0.0005 0.0005	Decreases clustering and coalescing.
Ethomeen S-15 plus Triton X-45	See Table 14	0.0005-0.001 0.0005-0.001	Prevents most clustering and coalescing.
Hodag 62-0	See Table 14	0.01-0.05	No effect.

Table 16. Effects of Surfactants in Both Sol and Dehydrating Medium on Sphere Formation

Sol	Dehydrating Medium	Remarks
0.002-0.02 vol % Igepal CO 990	0.4-0.6 vol % Bis-(2-ethoxyethyl) phthalate	Lower concentrations prevented coalescing, but not clustering, and caused some breakage. Higher concentrations prevented most clustering.
0.002 vol % Igepal CO 990	1.0 vol % butyl Carbitol	Prevented coalescing but not clustering.
0.01 vol % Ethomeen S-15	0.8 vol % of Bis-(2-ethoxyethyl) phthalate	Prevented coalescing and clustering.

Table 17. Effects of Surfactants on Preparation of Gram Quantities of Spheres

Surfactant[a]	Concentration (vol %)	Product Spheres	
		Quantity (g)	Percentage Yield
Alkanol OE	0.4	2.3	92
	0.6	1.9	94
	0.8	1.9	95
Alkanol HC	0.1	2.4	88
Alkanol OJ	0.1	2.2	72
Bis(2-ethoxyethyl) phthalate plus	0.6	2	93
Ethomeen S-15	0.04		
Bis(2-ethoxyethyl) phthalate plus	0.75	2	78
Ethomeen S-15	0.08		
Bis(2-ethoxyethyl) phthalate plus	0.8	1.1	88
Ethomeen S-15[b]	0.01		
Butyl Carbitol plus	1.0	1.6	74
Ethomeen S-15	0.4		

[a] Present in the dehydrating medium unless noted.

[b] Present in the sol.

% bis(2-ethoxyethyl) phthalate (to control clustering). After being dried overnight at 100°C and then heated to 170 to 180°C for 5 to 6 hr, about 88% of the spheres were found to be satisfactory (Table 17).

6. FIRING AND DRYING

Several of the gram-sized batches of microspheres, prepared by using some of the more promising surfactants, were calcined and reduced (Table 18). The spheres had thorium:uranium ratios ranging from 3:1 to 4.8:1. Most of the spheres had densities of greater than 95% of the theoretical densities of the oxide solid solutions, porosities of less than 1%, and oxygen:uranium ratios of less than 2.01. It required from 500 to greater than 2000 g to crush spheres that were 150 to 408 μ in diameter. Surface areas and carbon contents were measured in a few instances. The values obtained, respectively, were always less than 0.01 m^2/g, and from less than 0.01 to 0.001%. The oxygen:uranium mole ratio of 2.127 obtained for one batch of spheres could probably have been decreased by holding the spheres in the reducing atmosphere for a longer time. Another batch had a low density (92.2% of theoretical) and a porosity of 9.31%. Of the spheres fired, these were the only ones that had been made using 0.01 vol % Ethomeen S-15 in the sol; it is thought that this surfactant may have caused these seemingly anomalous values. Unfortunately, all the spheres were consumed in analysis, thereby preventing additional measurements.

All the spheres were formed by means of an electrostatic dispersing device,[16] which injected concentrated sol into a small column containing circulating 2-ethyl-1-hexanol and the required surfactants. The gelled spheres (Fig. 5) were removed from the column after 30 min; they were dried at a temperature of about 100°C for 16 hr and then at 170 to 180°C for 5 to 6 hr. The gelled spheres were initially dark red, and became black on drying. Usually, any possible breakage had occurred at this point. The normal firing schedule consisted of increasing the temperature to 1150°C in air, and then holding for 4 hr at this temperature in argon containing 4% hydrogen. Metallographs (at 100X and 500X) of typical thoria-urania microspheres are shown in Fig. 6. These spheres (sample 8 of Table 18) contained 71.88% thorium, 14.87% uranium, and 0.001% carbon, and had an oxygen:uranium mole ratio of 2.009, a mercury density of 10.12, and a surface area of 0.009 m^2/g. It required between 980 and 1560 g to crush spheres which were 240 to 300 μ in diameter. An x-ray examination showed a face-centered cubic pattern with a lattice parameter falling between that of UO_2 and ThO_2. Although the actual volume of calcined microspheres made in laboratory tests has been rather small, the production of spheres of this quality has successfully demonstrated the feasibility of microsphere preparation from sols made by the Amine Denitration Process.

Table 18. Specifications of Thoria-Urania Microspheres

	Spheres Prepared		Crush Strength Tests		Density				
Surfactant Conditions[a]	Quantity (g)	Yield (%)	Diameter (μ)	Resistance to Crushing (g)	Hg	Percentage of Theoretical	Porosity at 1 atm (%)	Oxygen: Uranium Mole Ratio	Thorium: Uranium Mole Ratio
1	2	93	255-357	1540-2000	10.03	98.2	<1	2.0044	3.52
2	2	78	204-306	940-1780	9.99	97.8	<1	2.0033	3.51
3	1.6	74	153-204	1180-1400	9.73	95.3	<1	2.0036	3.50
4	2.2	72	255-306	1600-2050	9.98	97.7	<1	2.0056	3.53
5	1.1	88	357-408	>2200	9.42[b]	92.2	9.31	2.0046	3.52
6	4.4	96	150-210	500-1150	10.12	99.1	<1	2.127	3.42
7	2.7	≥95	190-334	780-1240	9.98	97.4	<1	c	3.00
8	6	~50	240-300	980-1560	10.12	99.5	<1	2.009	4.82

[a] Surfactant conditions: In all eight conditions, the 2-ethyl-1-hexanol contains 0.5 vol % H_2O unless noted.

1. 0.6 vol % bis-(2-ethoxyethyl) phthalate and 0.04 vol % Ethomeen S-15 in the dehydrating medium.
2. 0.75 vol % bis-(2-ethoxyethyl) phthalate and 0.08 vol % Ethomeen S-15 in the dehydrating medium.
3. 1.0 vol % butyl Carbitol and 0.04 vol % Ethomeen S-15 in the dehydrating medium.
4. 0.1 vol % Alkanol OJ in the dehydrating medium.
5. 0.8 vol % bis-(2-ethoxyethyl) phthalate in the dehydrating medium and 0.01 vol % Ethomeen S-15 in the sol.
6. 0.03 vol % Span 80 and 0.04 vol % Ethomeen S-15 in the dehydrating medium.
7. 0.2 vol % Span 80, 0.1 vol % Ethomeen S-15, and 1.8 vol % H_2O in the dehydrating medium.
8. 20% octanol--80% 2-ethyl-1-hexanol used as the dehydrating medium.

[b] Hg density was an anomalous value; therefore, bulk density is reported.

[c] Not measured.

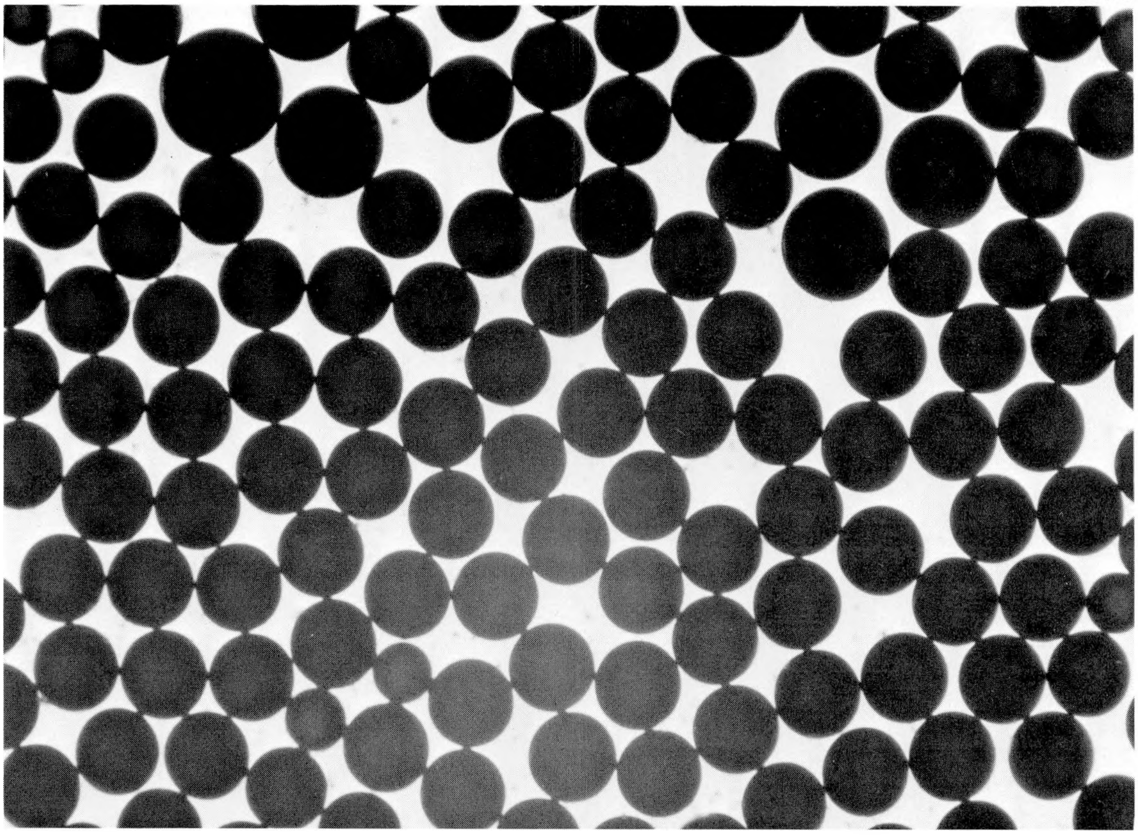


Fig. 5. Gelled Spheres Prepared from a Sol Made with the Amine Denitration Process.

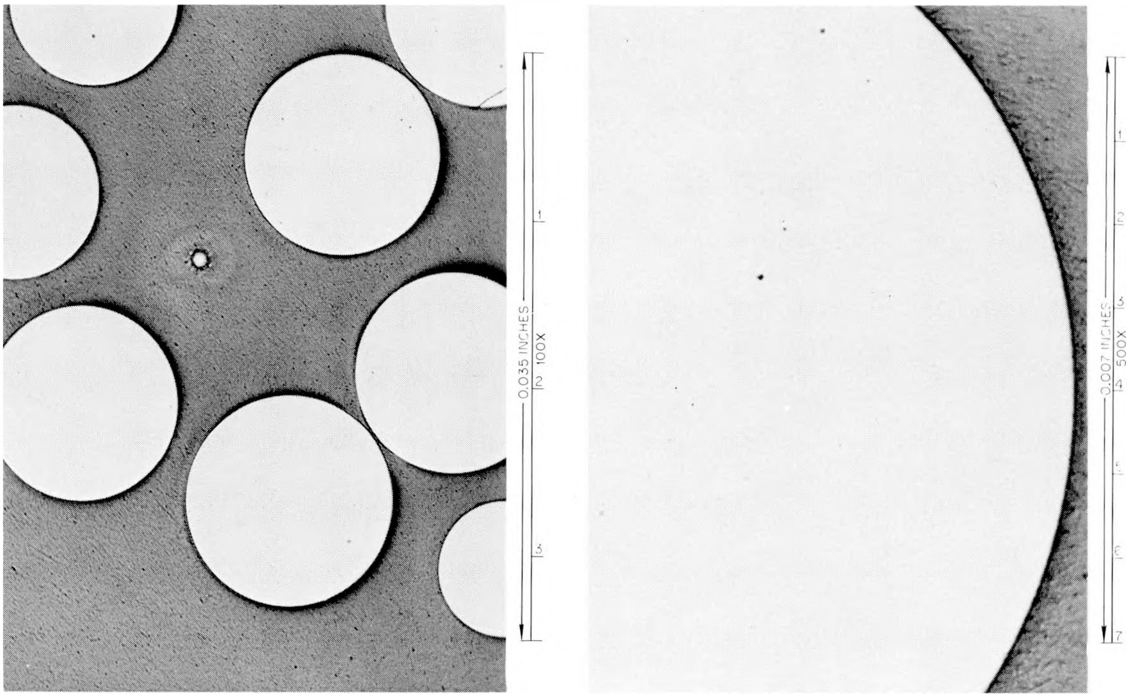


Fig. 6. Metallographs of Typical Thoria-Urania Microspheres Made from Sol Prepared by the Amine Denitration Process.

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9. APPENDIX

9.1 Single-Batch Extraction Technique

The earliest laboratory attempts to prepare sols by extracting nitrate with amines were made with a single-batch extraction technique. In this method the aqueous solution was contacted with the amine solution at elevated temperatures for 0.5 to 6 hr. The final nitrate:metal mole ratio approached a value of 0.2 asymptotically, and sols were formed that could be either evaporated to concentrated sols and formed into spheres or dried to gel fragments and calcined into products suitable for vibratory compaction. However, since the multiple-stage method proved superior, the single-batch technique was abandoned. The multistage process eliminated the necessity of conducting the extraction at aqueous reflux temperatures; the sols produced had more uniformly low amine:nitrate mole ratios; and the process was more amenable to scaleup and continuous operation.

As a typical example of the single-batch extraction process, an aqueous solution that was 0.215 M in thorium, 0.042 M in uranium, and 0.95 M in nitrate was contacted with 1 M Amberlite LA-2 in n-dodecane at approximately 100°C for 30 min. An amine:initial nitrate mole ratio of about 1.5 was used in this extraction. The resulting sol has a nitrate:metal mole ratio of 0.26.

Thorium nitrate--uranyl nitrate solutions with thorium:uranium ratios ranging from 1.1 to 11 were converted to sols having nitrate:metal ratios of from 0.2 to 0.3, using this batch extraction technique. Less than 0.01% of the thorium or uranium was extracted by the amine. Solutions that were 0.6 M or more in thorium formed solids during the first 3 to 5 min of denitration but liquefied after an additional 5- to 10-min contact with the amine at the elevated temperature.

A number of amines were screened as possible reagents for the process. The most acceptable sols were made with Amberlite LA-2, n-nonyldecylamine, Primene JM-T, and N-(1 nonyldecyl)benzylamine (Table 19). The latter had to be discarded since, after the denitration, the organic phase solidified on cooling and would be difficult to handle in a large-scale production. Amberlite LA-2 was chosen for the more-detailed studies. The n-nonyldecyl amine was a research chemical available only on special order; the Primene JM-T was not as easy to handle as the Amberlite LA-2. Several of the amines were discarded because of the large amounts of carbon they left in the sols (0.5 to 2 mg/ml). This high carbon content could prove to be a hazard during the calcining of shards for vibratory compaction. Triisooctyl amine gave an unusual sol; in that, about 30% of the uranium in the final product was reduced to U^{4+} (Table 19).

Table 19. Single-Batch Extraction Screening Tests

Feed: 0.12 M in thorium, 0.01 M in uranium, 0.50 M in nitrate

Amine:initial nitrate mole ratio = 2

Procedure: Contact aqueous 2 hr at reflux temperature with 0.5 M amine

Amine	Nitrate:Metal Mole Ratio
Primary:	
n-nonyldecylamine	
Batch 1	0.28
Batch 2	0.40
Primene JM-T	0.26
Secondary:	
Amberlite LA-1	0.67
Amberlite LA-2	0.26
Di-2-ethylhexylamine	0.67
Di-tridecyl P amine	0.39
N-(1-nonyldecyl)benzylamine	0.21[a]
Tertiary:	
Adogen 364	0.50
Alamine 336	0.55
Triisooctylamine	0.83[b]
Tri-n-octylamine	c

[a] Organic solidified after extraction.

[b] 30% of the uranium was reduced to U^{4+}.

[c] Third phase and extensive emulsions between phases.

Extractions were made at 60°C to reflux temperatures (101 to 104°C) for 15 min to 6 hr. There appeared to be little, if any, benefit of extending the contact time beyond 30 min if reflux temperatures were used. At 60, 80, and 90°C the nitrate:metal mole ratios, after contact with Amberlite LA-2, were 0.7, 0.6, and 0.3, respectively; at reflux temperatures, on the other hand, the ratio approached 0.2.

Many of the sols were dried to gels and calcined for 4 hr at 1150°C in air. When treated in this manner, thoria sols with nitrate:thorium mole ratios of about 0.3 had toluene densities of 9.81 to 9.95 and surface areas ranging from 0.02 to 0.004 m^2/g. The crystallite sizes of the gels, as determined by x-ray analysis, were about 40 to 50 A; and that of the fired shards ranged from 2000 to 2500 A. Similar (satisfactory) results were obtained with sols having a thorium:uranium mole ratio of 10:1.

9.2 Alumina and Zirconia Sols

Alumina and zirconia sols have been prepared using the single-batch extraction method. Approximately 0.1 M solutions of zirconium or aluminum nitrate were contacted for 2 hr at aqueous reflux temperatures with an excess of 0.5 M n-nonyldecyl amine in n-dodecane. From 1.6 to 2 moles of amine per mole of initial nitrate was used in this extraction step. The resulting zirconia sol was an opalescent, somewhat viscous liquid with a nitrate:metal mole ratio of 0.24. The alumina sol was slightly cloudy and had a nitrate:metal ratio of 0.33. This sol was dried to a gel at 100°C and then fired in air for 4 hr at 450°C. The fired oxide was a granular material with a surface area of 200 m^2/g and a density, as measured by toluene at 25°C, of 3.2577. X-ray studies indicated that the sol, the gel, and the fired oxide were amorphous.

9.3 Cleanup of Solvent

The first sols that were made by use of freshly prepared solutions of Amberlite LA-2 dissolved in n-dodecane contained as much as 0.8 mg of carbon (in an unspecified form) per milliliter. However, after the amine was used several times (i.e., had been regenerated by treatment with sodium carbonate and then reused in a denitration), the carbon in the sols decreased to a negligible level. For example, after an amine solution was used four or five times, the amount of carbon remaining in the sol was about 0.2 mg/ml or from 0.01 to 0.1 mg/ml, respectively.

To decrease the carbon content in the first sols that were made with an amine solution, the organic was subjected to a series of washings. These steps have not been optimized but are merely the ones used in the laboratory studies. The organic solution, usually 1 M amine in n-dodecane, was first washed with four volumes of 1 M Na_2CO_3. This prevented a permanent color change of the solution (which may or may not be harmful) after contact with aqueous nitrate solutions. Next, the solution was washed with 0.5 volume of H_2O to remove any entrained carbonate; then it was converted to the nitrate form with one volume of 2 M HNO_3. This amine nitrate was washed with five volumes of 0.1 M HNO_3 and one volume of H_2O, and was then reconverted to free amine with two volumes of 1 M Na_2CO_3. After being washed with one volume of H_2O, the organic was ready to use in sol preparation studies. Amberlite LA-2 solutions that had been washed by this procedure left only 0.07 to <0.01 mg of carbon per milliliter in the sols.

Washing removes part of the primary amine present in the Amberlite LA-2 (Table 20). The original amine contains about 4% primary, 94% secondary, and 2% tertiary. After washing, Amsco 125-82 solutions were 96.2% secondary. No attempt was made to determine why the washing results for some diluents were better than those of others.

Amberlite LA-2 solutions changed only slightly on prolonged usage. For example, a solution that had been used two months had about 1% more primary amine and 1% less secondary amine than a freshly prepared, washed solution. Infrared spectra of the initial and the aged solutions were identical; thus the 1% difference is probably within the precision of the analytical determination.

Table 20. Analysis of Amberlite LA-2

		Percentage Amine		
	M	Primary	Secondary	Tertiary
Amberlite LA-2 (Undiluted)				
Batch 1	2.23	4.13	93.95	1.92
Batch 2	2.23	3.91	93.91	2.18
Washed Solutions of Amberlite LA-2				
In Amsco 125-82	0.979	1.5	96.2	2.3
In diethylbenzene	0.994	0.2	99.7	0.1
In n-dodecane	0.606	0.66	97.36	1.98
Amberlite LA-2 in n-dodecane Used for Two Months	0.807	1.61	96.41	1.98

9.4 Losses of Uranium and Thorium During Extraction

A small amount of the uranium is extracted along with the nitrate in the extraction stages; however, these losses may be reduced to less than 0.05% by increasing the extraction time to 5 min and the extraction temperature to about 50°C (Table 21). Previous workers[13] showed that, in uranium--nitric acid--amine systems, uranium extraction decreases and nitric acid extraction increases with increasing temperature. Most of the uranium is extracted in the first stage, where the aqueous nitrate is higher. In the second stage the losses range from about 0.1% to less than 0.01%, depending on the extraction conditions. Thorium losses were less than 0.01% for all the extraction conditions used.

These sols were prepared with 0.75 M and 1.0 M solutions of Amberlite LA-2 in n-dodecane. A crosscurrent flow of 1.2 moles of amine per mole of initial nitrate was used to extract the nitrate from aqueous solutions that were 0.25 or 0.15 M in thorium nitrate--uranyl nitrate and in which about 17 mole % of the metal ion was uranium. Changes in any, or all, of the variables (time, temperature, and solution concentration) had little effect on nitrate extraction; in all instances the nitrate:metal ratios in the final sols were about 0.2, and the pH was about 4.6.

Uranium losses were reduced by increasing the amine concentration from 0.75 to 1 M (Table 21). However, the organic phase appeared to be more viscous and required slightly longer to separate than when the more dilute amine was used; thus 0.75 M is the recommended concentration.

Decreasing the feed concentration from 0.25 to 0.15 M in thorium plus uranium also decreased the uranium losses.

Table 21. Effects of Extraction Time and Temperature on Uranium and Thorium Losses

A. Conditions: 0.75 M Amberlite LA-2 in n-dodecane; crosscurrent flow
0.25 M thorium nitrate plus uranyl nitrate

Extraction Time (min)	Temperature (°C)	Uranium Losses (%)		Thorium Losses (%)
		First Contact	Second Contact	
2	20-25	1.3	0.1	<0.01
	50-60	0.5	<0.03	<0.01
5	20-25	0.54	0.06	<0.01
	50-60	0.06	0.02	<0.01

B. Conditions: 0.75 M in Amberlite LA-2 in n-dodecane; crosscurrent flow
0.15 M thorium nitrate plus uranyl nitrate

Extraction Time (min)	Temperature (°C)	Uranium Losses (%)		Thorium Losses (%)
		First Contact	Second Contact	
2	20-25	0.13	<0.01	<0.01
	50-60	0.03	<0.01	<0.01
5	20-25	0.06	0.01	<0.01
	50-60	<0.03	0.02	<0.01

C. Conditions: 1.0 M Amberlite LA-2 in n-dodecane; crosscurrent flow
0.25 M thorium nitrate plus uranyl nitrate

Extraction Time (min)	Temperature (°C)	Uranium Losses (%)		Thorium Losses (%)
		First Contact	Second Contact	
2	20-25	0.61	<0.01	<0.01
	50-60	0.07	<0.01	<0.01
5	20-25	0.30	0.01	<0.01
	50-60	<0.14	<0.01	<0.01

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