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THORIA SOL-GEL PROCESSES

PROCEDES SOL-GEL A LA THORINE

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Pinawa, Manitoba ROE 1L0
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RESUME

D'autres techniques de fabrication du combustible sont mises au point à l'établissement de Recherches Nucléaires de Whiteshell et font partie du programme du cycle combustible de la thorine. Les techniques sol-gel sont intéressantes et ce rapport tente de rassembler et résumer la myriade de renseignements relatifs aux combustibles provenant des procédés sol-gel à la thorine. Quelques renseignements de base sur le comportement et les avantages des formes de combustibles provenant des procédés sol-gel sont présentés et suivis d'un examen de la chimie des colloïdes y afférente et d'une explication des opérations fondamentales des procédés sol-gel. Plusieurs variantes du procédé de base sont enfin examinées et évaluées.

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ABSTRACT

Alternate fuel fabrication techniques are being developed at
WNRE as part of the thorium fuel cycle program. The sol-gel techniques
are attractive and this report assembles and summarizes information
relating to thoria sol-gel fuels. Some background information on the
behaviour and advantages of sol-gel fuel forms is presented, followed by
a review of relevant colloid chemistry and an explanation of the funda-
mental steps of sol-gel processes. Finally, several variants to the
basic process are reviewed and evaluated.

CONTENTS

1. INTRODUCTION

An integral part of the thorium fuel cycle will be an active fuel fabrication facility *to render recycled* ^{233}U into a mixed oxide $(Th,U)O_2$ fuel compatible with the reactor system. WNRE will be evaluating the fabrication techniques and irradiation performance of sol-gel powder-packed and extruded fuels as part of AECL's advanced fuel cycle program. The program objectives and rationale have been discussed by Hatcher[1] and a major undertaking will be development of methods for active fuel fabrication in a remote, shielded facility. Even though a significant amount of work has been done on sol-gel fuels and pilot plants are operating throughout the world, no sol-gel process has reached the commercial production stage.

During the irradiation of thorium and ^{233}U, the uranium isotope, ^{232}U, is formed. The daughters of this uranium isotope emit highly penetrating gamma radiation. This necessitates that fabrication operations be done remotely behind heavy shielding[2]. Fabrication in a remote facility will be difficult and any recycle fuel fabrication process adopted must be highly reliable. This implies that the process must be simple, should be nearly dust free and should generate only small amounts of waste. Several variants to the basic sol-gel process have been developed and they should be evaluated in light of the above requirements before a commitment to a sol-gel pilot plant is made.

This report introduces the basics of *sol-gel technology and reviews the various sol-gel techniques*. Some background information on sol-gel fuels will be presented, followed by a simplified review of pertinent colloid chemistry and a qualitative rationalization of the fundamental steps of the sol-gel processes. Finally, *the most interest-*

ing modifications of the basic process will be reviewed. This report
is intended to serve as a basis for evaluating the processes with a view
to identifying any further development work required. Basically our
approach will be to duplicate and modify the work done at the Oak Ridge
National Laboratory (ORNL) during the early sixties and bring our
expertise to the point where we can make a sound judgement on the
advisability of continuing a sol-gel fabrication technique to the pilot
plant stage.

2. BACKGROUND

2.1   MERITS OF SOL-GEL PROCESS

The sol-gel techniques developed for nuclear applications at
laboratories in the Netherlands, Italy and the United States seem to
overcome some of the difficulties of remote fabrication. Sol-gel fabrica-
tion techniques offer several advantages over standard pelleting:

   i)   The fuels are made via a wet chemistry route thereby
         avoiding dust-generating steps.
   ii)   The fabrication equipment is relatively simple thereby
         reducing some maintenance problems.
   iii) The processes use uranyl nitrate directly from the re-
         processing plant thereby eliminating the conversion to
         sinterable UO_2.
   iv)   The green fuel can be sintered to high density at rela-
         tively low temperatures ($\sim 1200°C$) thereby eliminating
         high temperature ($1700°C$) sintering furnaces.

Opposing these advantages are the difficulties of introducing
a new and unproven technology and verifying that the irradiation be-

haviour of a new fuel configuration is acceptable in CANDU* reactors. This is no small barrier to overcome and considerable development will be necessary before a sol-gel process is adopted.

2.2 SOL-GEL FUEL FORMS

Sol-gel derived fuels can be fabricated in several forms as shown in the flow sheet in Figure 1. Vipac fuel consists of angular particles, usually less than 1000 µm in diameter, which are mixed and vibration-compacted into fuel elements to densities approaching 90% of theoretical (90% T.D.). Spherepac fuel consists of a two- or three-size mix of nearly perfect spheres (<1000 µm) vibration-compacted into fuel elements up to 90% T.D. Vibration-compaction of spheres to high density is well understood both theoretically and practically (3,4). The problem becomes one of making high density coarse- and fine-sized spheres with a uniform size distribution. Extruded fuel consists of rods up to 150 mm long extruded from sol-gel derived clays. Pellet fuel is pressed from finely ground sol-gel shard.
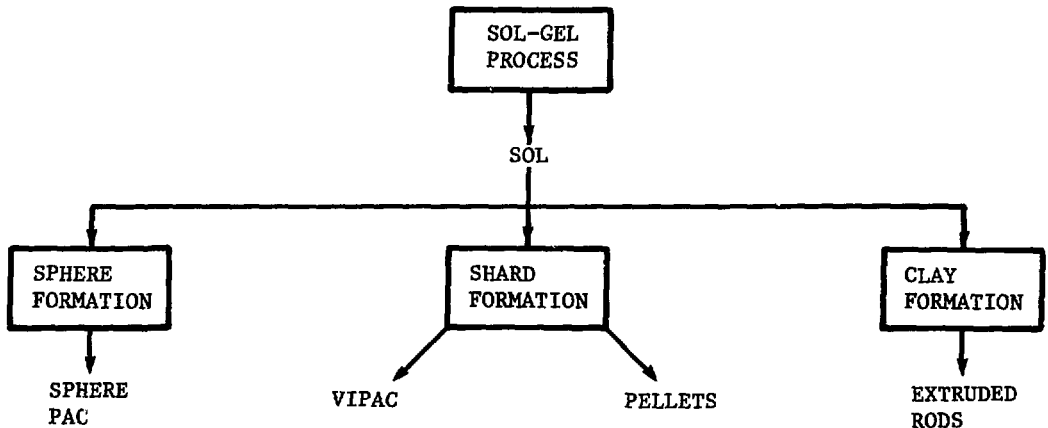

FIGURE 1: FLOW SHEET FOR SOL-GEL-DERIVED FUEL FORMATS

* CANada Deutrium Uranium

Most of the nuclear laboratories throughout the world have
concentrated their sol-gel development work on spherepac fuels. An
enormous amount of detailed information was generated in the United
States in support of the thorium fuel cycle studies. Unfortunately
this work has been phased out. Nevertheless, the reference fuel for
high temperature gas-cooled reactors is sol-gel-derived, coated-particle
fuel and several countries are actively engaged in sol-gel development
studies. Currently, the reference route for fabricating recycle $(U,Pu)O_2$
fuels is conventional pelleting; however, most interested countries are
carrying out development work on spherepac fuels.

For example, the United Kingdom has a development program for
spherepac fuel for the fast breeder, Belgium has fabricated and irradiated
spherepac $(U,Pu)O_2$ fuel and the Federal Republic of Germany has developed
spherepac fabrication facilities for their fuel cycles. There seems to
be general agreement that the sol-gel route would offer advantages over
pelleting for fabricating mixed oxide fuels.

2.3   IRRADIATION BEHAVIOUR

Irradiation experience with powder-packed thoria fuels has
been somewhat sparse, but experience indicates that the irradiation
behaviour is probably acceptable[5]. Initially spherepac fuel will
operate at higher temperatures than pellet fuel because of its lower
fuel density and thermal conductivity. After irradiation-induced
sintering, the fuel restructures and behaves similarly to pellet fuel
with a central void. Fission gas release for spherepac fuel, because
of its higher specific surface area and higher operating temperature,
should be somewhat greater than for pellet fuel. The number of defects
occurring in spherepac fuel should be no greater than in pellet fuel,
however, there could be a potential waterlogging problem[6,7].
Spherepac fuel should decrease the severity of fuel-clad interactions
since elements will not be subject to ridging at pellet interfaces.

Spherepac fuel will probably require free-standing, thick wall sheathing and the additional neutron adsorption combined with low density fuel may annul the self-sustaining thorium cycle. The irradiation program for spherepac fuel will study these problems.

The irradiation behaviour of extruded fuel with large length-to-diameter ratios (L/D $\geq$ 10) has never been studied to any extent. Chalder[8] reported on the irradiation behaviour of extruded UO_2 and concluded that circumferential ridges did not appear in single rod elements ($\sim$ 95 mm long). Uranium carbide fuel is loaded into fuel sheaths in random lengths between 40 and 150 mm and no performance limitations have been noted[9]. The experiments showed that dishing was unnecessary and, in fact, dishes tended to promote circumferential ridging. The case with oxide fuel may be somewhat different. Veeder[10] calculated that radial expansion at the end of a cylinder increases with increasing L/D. Carter[11] showed that, in irradiated UO_2, pellet chipping, element bowing and circumferential ridging were greater with L/D ratios of 1.5 than for L/D ratios of 0.5, however, the ridging was probably related to the presence of dishes and extruded rods will be flat-ended.

3. BASIC CHEMISTRY OF SOL-GEL PROCESSES

3.1 DEFINITION OF TERMS

Some of the fundamental properties of thoria sols and gels were studied when the homogeneous slurry type of reactor containing an aqueous suspension of mixed oxides was being considered[12,13,14]. While some of the data seem inconsistent, sufficient information is available to make a qualitative rationalization of the stability of thoria sols based on a simplified colloid stability theory. Even though the following model is based on a naive interpretation of the

available information, it should form a basis for understanding sol-gel processes and also act as a starting point for more sophisticated explanations.

A sol is a stable colloidal suspension of small (1.5 to 20 nm) crystallites in an aqueous medium. The particles exhibit Brownian motion but remain suspended for a finite time. Peptizing refers to the stabilization of colloid sols by the addition of electrolytes or peptizing agents which provide ionic charges surrounding each particle. A gel is a viscous, jelly-like sol which possesses sufficient elastic strength to retain its shape. The crystallites create an open structure containing entrapped water and Brownian motion ceases. Sols set into gels without any apparent property changes. For example, thixotropic gels convert to sols with agitation then revert to gels on standing. The term flocculation refers to the nucleation and growth of particles and the subsequent settling out of solution.

3.2   NATURE OF DISPERSION FORCES

The nature of the interparticle dispersion and flocculation forces forms the basis of colloid stability. Figure 2 plots the potential energy for the interaction between two colloidal particles as a function of separation distance. London-type attractive forces are counterbalanced by electrostatic dispersion forces so the net potential energy for the system is given by the sum of the two terms. At a separation distance corresponding to V_m, the repulsive forces dominate and stable sol conditions exist. This potential energy barrier must be overcome before London building can predominate and when it is overcome, say by thermal energy, the particles will flocculate and drop out of the sol. Flocculation is usually irreversible. The attractive forces are the classic London - van der Waals bonding and can be estimated using the Hamaker method[15]. The repulsive forces are electrostatic in nature and can be estimated with the Deryaguin-Landau-Verwey-Overbeck
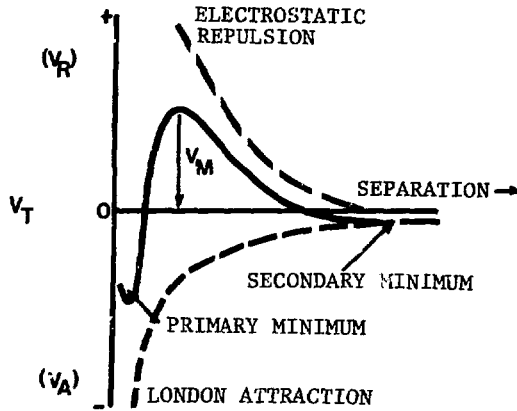
FIGURE 2: TOTAL POTENTIAL ENERGY (V_T) DIAGRAM FOR TWO COLLOIDAL
          PARTICLES

theory[15,16]. The mathematics of the D-L-V-O theory are beyond the
scope of this report but the theory forms a quantitative explanation of
colloid stability.

        The origin of the electrostatic repulsive forces stems from
the surface charge of the suspended particle and the surrounding atmos-
phere of the counter ions necessary to neutralize the surface charge.
These electrostatic forces are strong enough to both repel particles and
overcome gravity effects as illustrated in Figure 3. The potential of
the electrical double layer is dependent on ionic strength and the pH of
the liquid suspension. Peptizing ions are strongly adsorbed on the part-
icle surface thereby increasing the strength of the electrical double
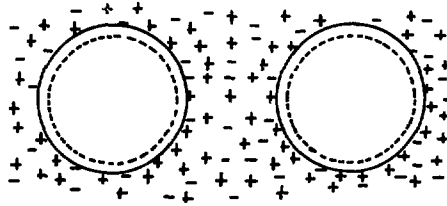layer surrounding each particle.

FIGURE 3: INTERACTION OF TWO ELECTROSTATICALLY STABILIZED PARTICLES

3.3   NATURE OF THE ELECTRICAL DOUBLE LAYER IN THORIA SOLS

The surface of a freshly fractured or newly formed oxide particle
will be distorted on the atomic scale because the cation and anion balance
is destroyed. The lattice irregularity due to unsatisfied surface bonds
is schematically represented in Figure 4. Depending on the surface plane
exposed and the predominating ion, the surface will become negatively or
positively charged. In the presence of water, the surface aligns the
dipoles of the water molecule which are then attracted to the surface.
Thoria surfaces can exhibit both negative and positive charges, but
generally prefer to adsorb anions[12]. Surface charge in an aqueous
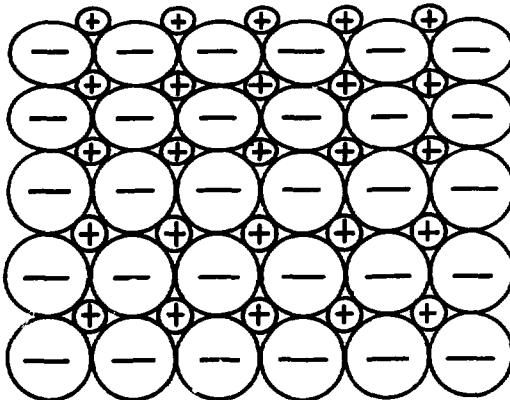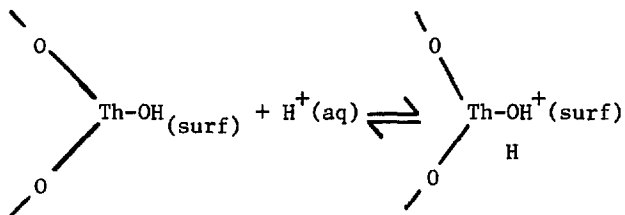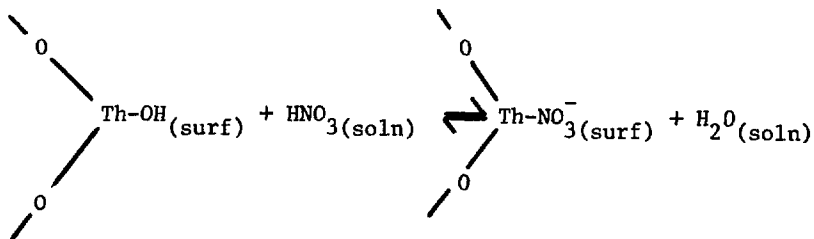solution is established by surface hydration followed by dissociation of

FIGURE 4: SCHEMATIC REPRESENTATION OF THE ATOMIC OR IONIC
DISTRIBUTION IN THE SURFACE REGIONS OF CRYSTALS

the surface hydroxide. This leads to a positive charge in the following manner:

$$\diagdown O \diagdown\diagup Th\text{-}OH_{(surf)} + H^+(aq) \rightleftharpoons \diagdown O \diagdown\diagup Th\text{-}OH^+(surf)$$

A negative charge is established when the surface hydroxyl dissociates. This explains the sensitivity of oxide hydrosols to pH. In each case surface hydroxyl groups are produced and the adsorbed ionic units attract counter ions so that an electrical double layer exists in the immediate vicinity of the particle. This, in effect, creates a hydrosphere of rigidly held liquid with properties different from water. This hydrosphere controls some of the important properties of thoria sols and gels.

Thoria sols are stabilized and peptized by the addition of dilute nitric acid and adsorption studies have shown that thoria adsorbs a finite amount of ionic nitrate on preferred sites[17]. Thoria sols are usually formed from either hydrous, amorphous thoria prepared by precipitation from thorium nitrate or from crystalline thoria prepared from steam-denitrated thorium nitrate. Both types will have the hydrated surface discussed above and, in addition, some residual adsorbed nitrate ions. The stablization of thoria sols by HNO_3 can be rationalized by an anion exchange mechanism where the nitrate ion exchanges with the surface hydroxyl in the following manner:

$$\diagdown O \diagdown\diagup Th\text{-}OH_{(surf)} + HNO_{3(soln)} \rightleftharpoons \diagdown O \diagdown\diagup Th\text{-}NO_{3\,(surf)}^- + H_2O_{(soln)}$$

This ionized surface nitrate leads to the strong electrical double layer needed for suspension of thoria sols. A possible schematic for the double layer is shown in Figure 5, where the potential energy surrounding the particle decreases as distance from the particle increases. The zeta potential represents the electric potential in the double layer at some unknown distance from the particle surface corresponding to the shearing plane interface between the bulk liquid and the hydrosphere. The magnitude of the zeta potential is a measure of the repulsive strength between particles. The zero point of charge (ZPC) occurs at a pH of the sol which corresponds to a zero surface charge. An understanding of zeta potential and ZPC is essential to explaining the nature of thoria sols.
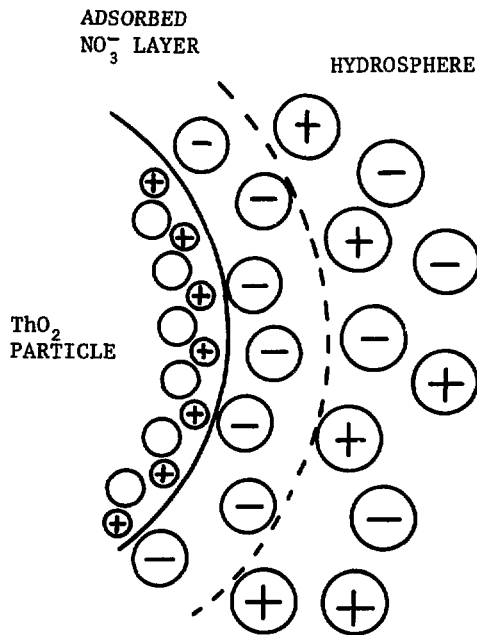

FIGURE 5:   IDEALIZED SCHEMATIC OF ELECTRIC DOUBLE LAYER

It must be emphasized that Figure 5 is a simplified model and several other combinations of adsorbed units could be rationalized depending on the exposed crystal face and the acidic or basic nature of the solution. Olson et al[18] used infrared spectroscopy to identify some of the chemisorbed species on thoria gels, and discussed likely surface adsorption models.

3.4 CHARACTERISTICS OF THORIA SOLS AND GELS

The colloidal properties of thoria sols are dependent on the strength and nature of the electrical double layer which, in turn, is sensitive to the pH of the solution and any ionic species present in the solution. Thoria sols and gels exhibit various viscous properties depending on thoria concentration, nitrate concentration, ageing effects and shear velocity[19]. Work at ORNL[20] has shown that thoria crystallites form into elongated flocs. Simple schematic representations of possible modes of particle association are shown in Figure 6. The sol consists of discrete particles mutually repelled by electrostatic forces.

a) DISPERSED   b) GELLED   c) FLOCCULATED

FIGURE 6:   PARTICLE INTERACTIONS IN SOLS AND GELS

A gel forms by London-bonding at particle edges, thereby enclosing a large
volume of water but forming a rigid structure. The flocculated structure
is formed when the gel structure collapses and London bonds are formed at
particle edges and faces. The flocculated structure holds a significant
volume of water. The viscosity and rheological behaviour of colloids are
governed by the amount and type of particulate bonding.

Thoria fuels will contain reprocessed ^{233}U which can be mixed
with thoria sols as a uranyl nitrate solution. Uranium (VI) ions readily
adsorb on the surface of thoria particles[21] and may even enhance the
strength of the electrical double layer. The resulting sol contains a
suspension of $ThO_2 \cdot UO_3$ particles, which turns into a homogeneous mixed
oxide fuel after gelation, drying and firing.

3.5   FUNDAMENTAL SOL-GEL FABRICATION STEPS

Nearly all thoria sol-gel processes can be broken into three
basic steps:

- preparation of a stable oxide sol,
- gelation of the sol into a useable shape,
- drying and sintering into a high density, mixed oxide fuel.

The sol preparation step starts with removal of the nitrate ion
from thorium nitrate and the subsequent formation of submicron hydrated
thoria crystallites. The thoria crystallites are dispersed in an
aqueous solution containing a peptizing ion. The sol is then concentrated
to the molar concentration needed for the end use (extrusion or sphere-
pac). Techniques for hydrosol preparation include:

- hydrothermal denitration of thorium nitrate followed by
  peptizing with nitrate ion,

- precipitation of thorium hydroxide with ammonia followed by peptizing,
- removal of the nitrate from thorium nitrate by amine extraction.

The peptizing ion derives from the amine extraction technique by incomplete extraction of the nitrate.

The first fuel charge for the consuming thorium cycle is envisaged to contain thoria enriched with plutonium; subsequent charges will contain recycled UO_2 and PuO_2 topping mixed with ThO_2. These mixed oxide fuels are formed during the sol preparation step. Plutonia sols are compatible with thoria sols and can be formed by the precipitation – peptization process or by solvent extraction, and mixing with the thoria sol. Up to 10% ^{233}U can be added to thoria sols by using nitrate as the source of the peptizing ion.

The gelation step transforms the dilute sol into a more concentrated gel that has the desired final shape of the mixed oxide fuel. Gelation is accomplished either by dehydration of the sol or lowering the surface potential of the dispersed crystallites. Dehydration flocculates the sol by removing some of the suspending liquid, thereby decreasing the distance between particles and initiating attractive forces at particle edges. Water can be removed by thermal treatment as in shard formation where the sol is dried in trays, or as in clay formation where flocculation is initiated by water evaporation and filtration. The most common gelation technique is carried out by dispersing sol droplets into a water-soluble alcohol which forms discrete gelled spheres.

Alternatively, gelation can be effected by removal of the stabilizing nitrate ion by increasing the pH of the sol. This method reduces the strength of the electrical double layer, thereby allowing attractive forces to dominate. Internal gelation occurs during sphere

formation when ammonia is released from a temperature-sensitive donor added to the sol. During the solvent extraction process the pH is increased by further acid extraction with primary amines. The gel-supported precipitation process avoids the sol preparation step by mixing organic additives with a thorium nitrate solution. This solution is injected directly into a microsphere-forming column filled with ammonia so that sol formation, gelation and spheriodizing are accomplished in one step.

The final steps for microsphere production are washing and drying the gelled spheres to remove water, nitrate and organic contaminants, followed by sintering to high density. Substantial shrinkage occurs during thermal treatment so drying and sintering must be done carefully. Thoria gels can be densified to > 99% T.D. at ∿ 1200°C. This high degree of sinterability at relatively low temperatures is thought to be due to the dense packing of very fine thoria crystallites[22]. Prolonged annealing at 1800°C causes pore growth and subsequent density decreases in thoria sol-gel spheres[23].

The alternate sol-gel routes are summarized in the flow sheet in Figure 7. These routes form the basis for various sol-gel fuel fabrication methods for mixed oxide spherepac fuel developed throughout the world. The variants will be discussed in more detail in the next section.

4. SOL-GEL FABRICATION

4.1 DENITRATION-PEPTIZATION TECHNIQUE

Sol-gel processes have been developed for UO_2, PuO_2 and ThO_2, but only the thoria processes will be considered. Ferguson[21] and Haas[24] discuss in detail the denitration-peptization technique developed at ORNL for fabricating $(Th,U)O_2$ microspheres. Figure 8 shows the
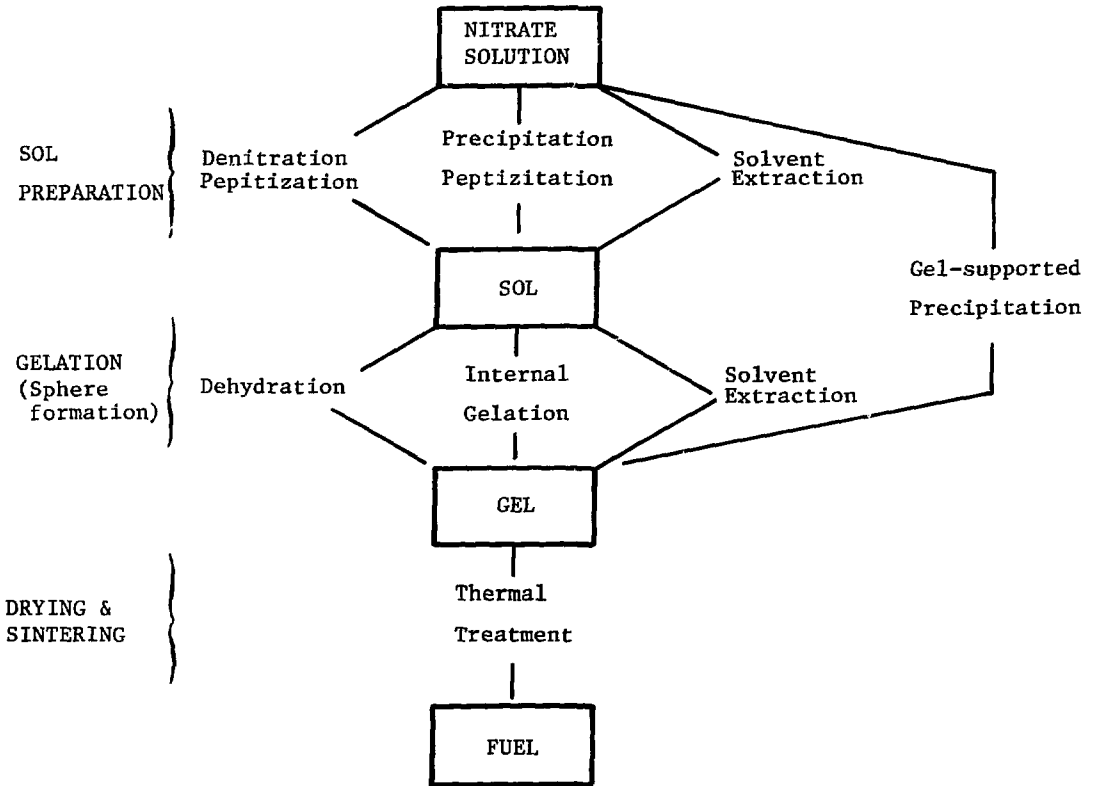
FIGURE 7: SCHEMATIC FLOW SHEET OF THE FOUR
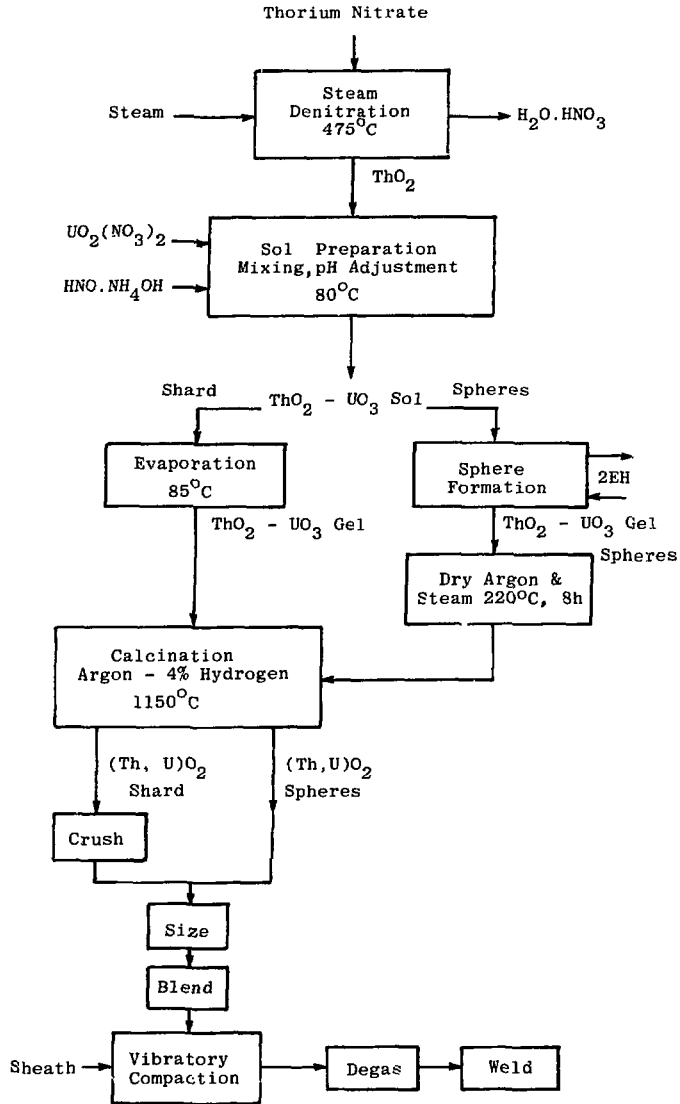THORIA SOL-GEL PROCESSES

FIGURE 8: PROCESS FLOW SHEET FOR FABRICATION OF (Th,U)O$_2$ POWDER-
PACKED FUELS VIA THE DENITRATION-PEPTIZATION TECHNIQUE.

process flow sheet developed at ORNL for the Kilorod Project[25], which
was a successful demonstration of a medium-sized remote facility for the
production of (^{233}U, Th)O$_2$ fuel rods. The first step is conversion of
thorium nitrate into a dispersible oxide by hydrothermal denitration
according to the reaction

$$Th(NO_3)_4 \cdot 4H_2O + 2H_2O_{(g)} \rightarrow ThO_2 + 4HNO_3 + 4H_2O$$
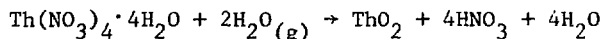
The reaction is carried out in a rotating calciner under steam preheated
to 475°C. The dispersibility of the thoria is sensitive to the nature
of residual nitrate and surface hydroxyl units so heating rates must be
carefully controlled. For example, the endothermic reaction occurs at
200°C and rapid heating will cause improper nitrate decomposition and an
unstable thoria sol.

The sol preparation step consists of mixing the thoria with
uranyl nitrate and sufficient nitric acid to suspend the thoria crystal-
lites. The ORNL work showed that an NO$_3$:Th mole ratio of 0.08 gave a
stable sol and high density spheres. Peptizing is complete after 30
minutes mixing at 80°C after which the pH is adjusted to 3.9 with am-
monia. The acidic sol apparently dissolves the uranium so the pH must
be raised to allow complete adsorption on the thoria crystallites.
Using properly denitrated thoria, ORNL reported 99.5% dispersibility
with this technique[21].

Gelation is accomplished either by dehydration of the sols in
trays and crushing the dried cake into shard or by water extraction in
microsphere-forming columns. ORNL has developed the technique for
transforming thoria sol into gelled spheres[26]. The process consists
of injecting sol droplets into 2-ethyl-hexanol (2EH) flowing up through
a tapered glass column. The sol droplets fluidize in the flowing 2EH
and spheroidize due to surface tension effects. As the spheres drop
through the column, water is extracted and the spheres gel and shrink.

The size of microspheres can be varied by controlling sol concentration, injection geometry and flow conditions. The sphere formation process is an art itself and further details can be found in the references. The spheres are then dried in steam and argon at 220°C and sintered to >99% T.D. at 1200°C. The gelled spheres are composed of ThO_2 and UO_3 so sintering is carried out in hydrogen to reduce UO_3 to UO_2. The sintered spheres are sized to obtain a two- or three-size mix with the optimum packing efficiency, and vibration-compacted into fuel elements.

The sol-gel extrusion process was developed at ORNL[27] and is a variant of the denitration-peptization process. The sol is changed into a clay by increasing the nitrate-to-thorium ratio to 0.16 and concentrating the sol by evaporation until flocculation occurs. The higher nitrate ratio will increase the surface charge on the thoria crystallites and produce a more stable sol. Apparently the higher surface charge affects the nature of the flocculated structure and the concentrated clay-like gel results. Filtering the gel reduces the water content to about 20% and the final clay is suitable for extrusion. A possible flow sheet for thoria sol-gel extrusion is shown in Figure 9. After extrusion the rods are cut off, dried under controlled conditions to avoid surface cracking and distortion, then sintered at 1200°C to about 98% T.D. A final end grinding step should lead to rods about 150 mm long, ready for loading into fuel elements.

4.2   SOLVENT-EXTRACTION TECHNIQUES

The uranium concentration in mixed oxides produced via the hydrothermal denitration route is limited to about 10%, while liquid-liquid extraction techniques can increase the uranium concentration to 30%. Basically, thorium nitrate plus uranyl nitrate solutions are converted directly into sols by extracting the nitrate with amines. The flow sheet in Figure 10 outlines the basic process developed at ONRL[28]. A dilute sol is formed after two extractions with Amberlite LA-2 in the
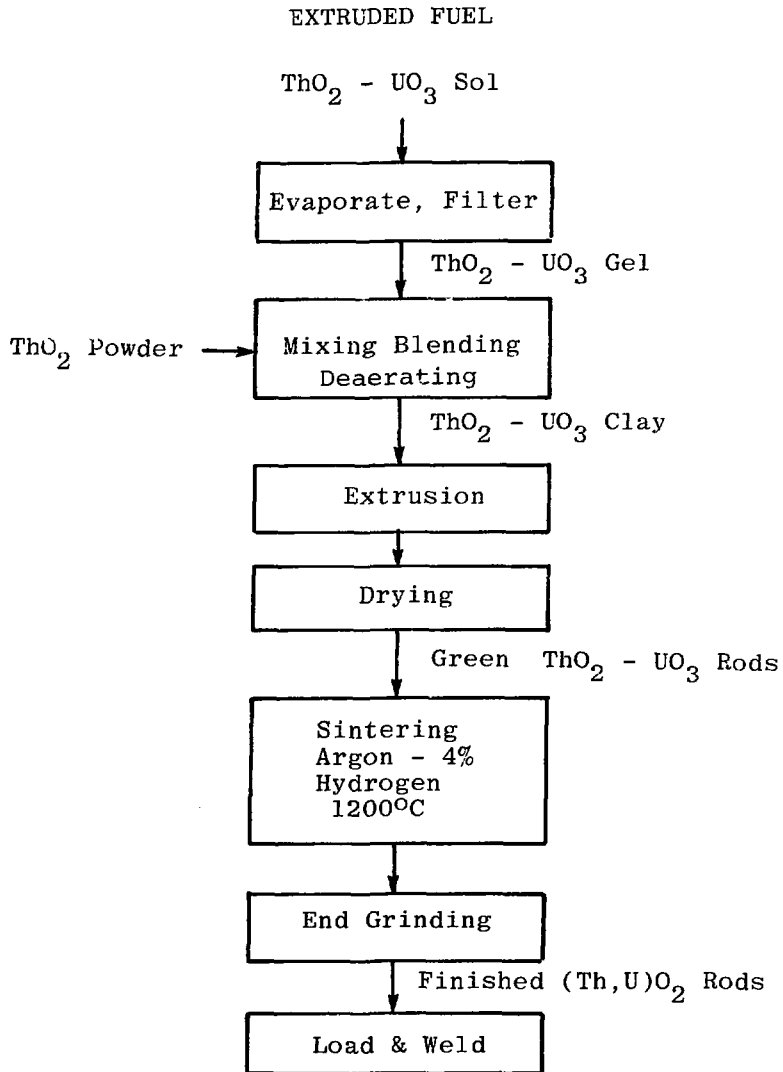
EXTRUDED FUEL

$ThO_2 - UO_3$ Sol

↓

| Evaporate, Filter |

↓ $ThO_2 - UO_3$ Gel

ThO_2 Powder → | Mixing Blending Deaerating |

↓ $ThO_2 - UO_3$ Clay

| Extrusion |

↓

| Drying |

↓ Green $ThO_2 - UO_3$ Rods

| Sintering Argon - 4% Hydrogen 1200°C |

↓

| End Grinding |

↓ Finished $(Th,U)O_2$ Rods

| Load & Weld |

FIGURE 9: PROCESS FLOW SHEET FOR SOL-GEL EXTRUSION OF $(Th,U)O_2$ FUELS.

mixer-settlers. The sol is then concentrated by evaporation and injected into the microsphere-forming column. Although the process looks simple, one disadvantage seems to be the high residual nitrate concentrations after the second extraction.

The C.N.E.N.* laboratories in Italy have developed a solvent-extraction sol-gel technique using Prime JMT as the extractant[29]. The C.N.E.N. process eliminates the need for a low residual nitrate in the sol since a final acid extraction takes place during the gelation step. This is accomplished with amine additions to the sphere-forming column followed by thorough washing of the gelled spheres to remove residual ammonia. The technique seems particularly suitable for producing high density fine spheres (10 to 100 μm).

4.3   PRECIPITATION-PEPTIZATION TECHNIQUE

The internal gelation technique has been developed at the KEMA[†] laboratories in the Netherlands[30] and a process flow sheet is shown in Figure 11. Thoria sols are prepared by precipitating thorium hydroxide from a thorium nitrate solution with ammonia. The precipitate is washed to remove ammonia, peptized with nitric acid or uranyl nitrate and concentrated for the gelation step. Microspheres are formed by emulsifying the sol with a high frequency vibratory mixer in carbon tetrachloride. This technique is particularly good for making very small spheres. Gelation is effected by increasing the pH of the sol droplets by diffusion of ammonia from the gelation liquid into the gel drops. Large spheres are made by injecting sol droplets into gelation towers. Internal gelation of the spheres is accomplished with an ammonia donor (urea) added to the sol and released by the hot gelation liquid. The gelled spheres are then washed to remove ammonium nitrate, dried and sintered to high density.
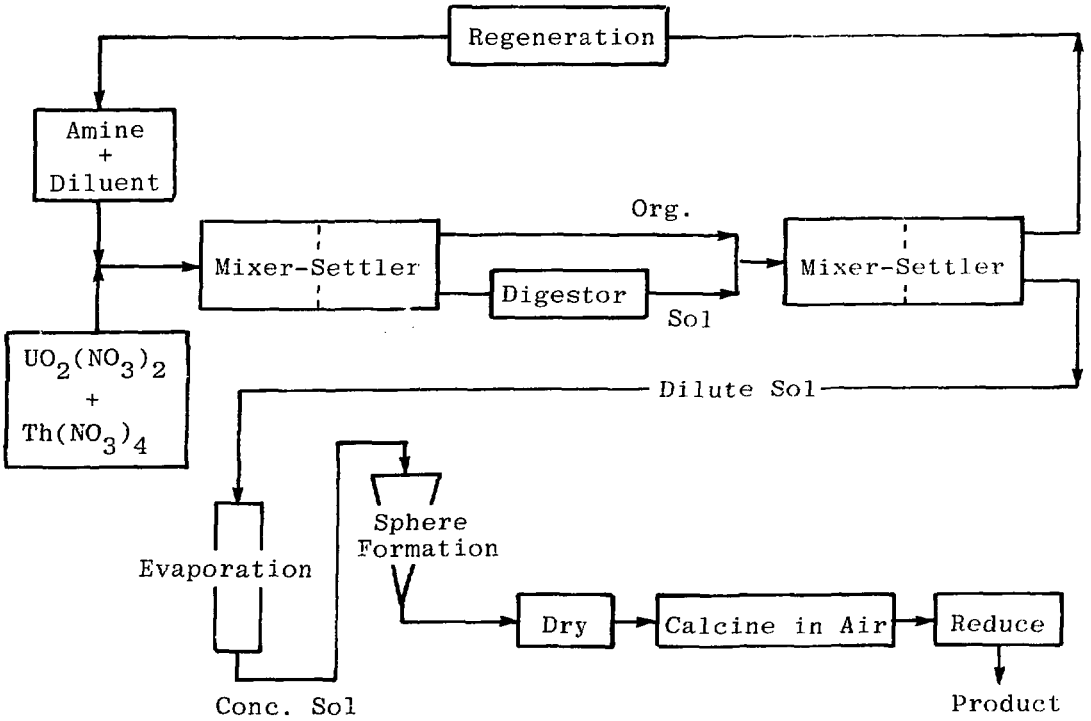

FIGURE 10:   PROCESS FLOW SHEET FOR PREPARATION OF $(Th,U)O_2$ MICROSPHERES VIA LIQUID-EXTRACTION PROCESS.
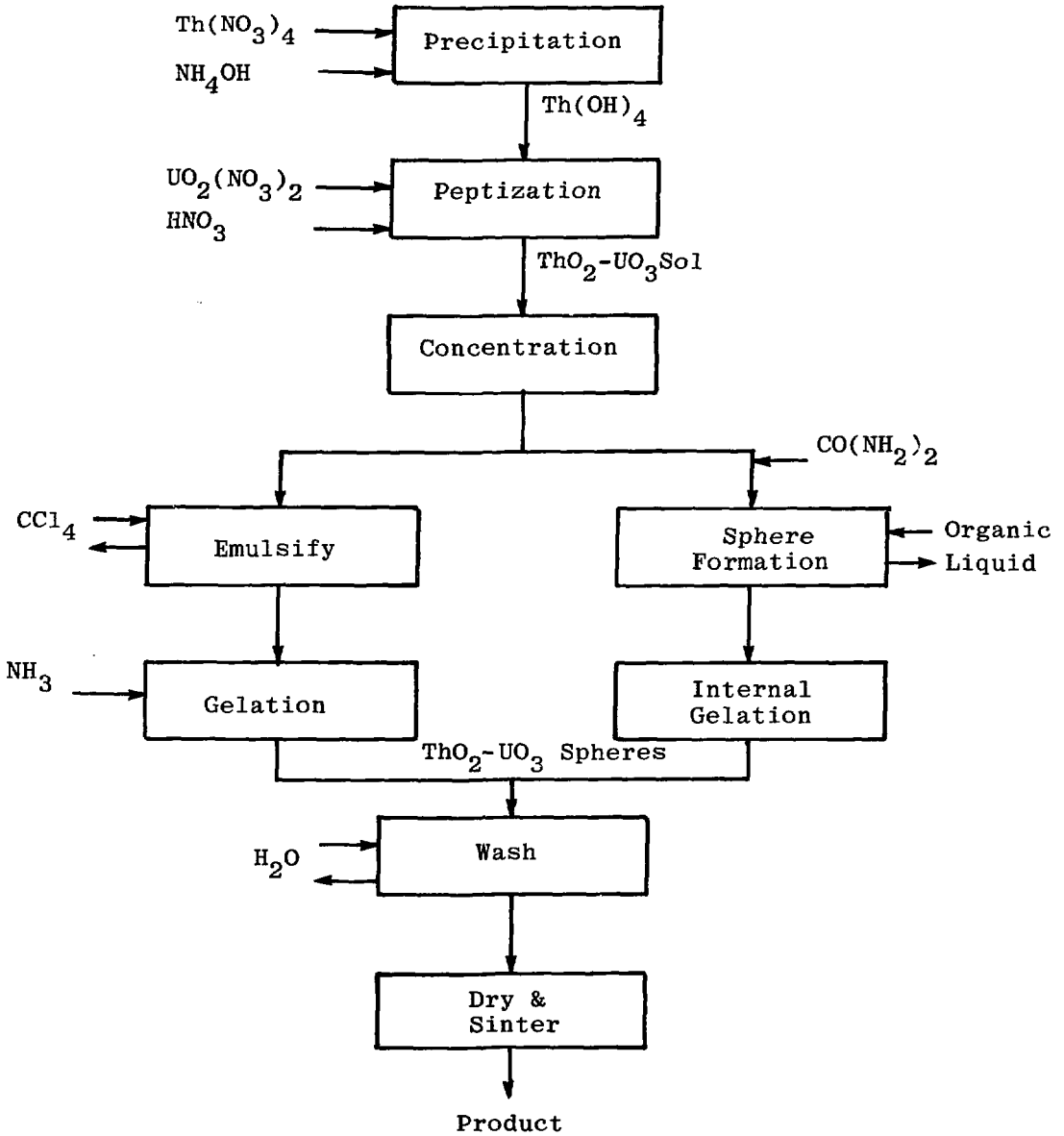
FIGURE 11: PROCESS FLOW SHEET FOR PREPARATION OF $(Th,U)O_2$ MICROSPHERES VIA PRECIPITATION-PEPTIZATION PROCESS.

4.4   GEL-SUPPORTED PRECIPITATION

The most recent variant to sol-gel technology is the gel-supported precipitation process developed at SNAM Co. in Italy[31]. The process uses a cellulose resin to thicken the starting nitrate solution and combines the sol preparation and gelation steps as shown in the flow sheet in Figure 12. During the first step, a thorium nitrate solution is partially hydrolyzed with concentrated ammonia and this solution is mixed with methocel. The sol is then dripped into an ammonium hydroxide solution where gelled spheres are supported by the methocel as they precipitate out of solution. The spheres are then aged in ammonia to complete the gelation and washed to remove residual ammonium compounds. The spheres are dehydrated in a solvent, then dried and sintered at 1350 to 1450°C. The process is particularly useful for producing coarse spheres.

5. SUMMARY

Prior to embarking on a pilot plant facility, it would seem wise to evaluate the four main variants to the sol-gel processes. Nevertheless, firsthand experience will probably be needed to decide whether any one technique is clearly superior in cost, performance or simplicity. Since thorium cycles in CANDU reactors are sensitive to fuel density, two important criteria will be individual sphere size and density. Other considerations are the adaptability of the process to remote operation, time-consuming steps, reliability of the process, reproducibility of the final product, the volume of wastes generated, and the ability to use the process with the high uranium concentrations that will be necessary if denatured cycles are to be used as a means of avoiding nuclear weapons proliferation. Finally, the amount of world experience on a particular process will weigh heavily on its appeal.
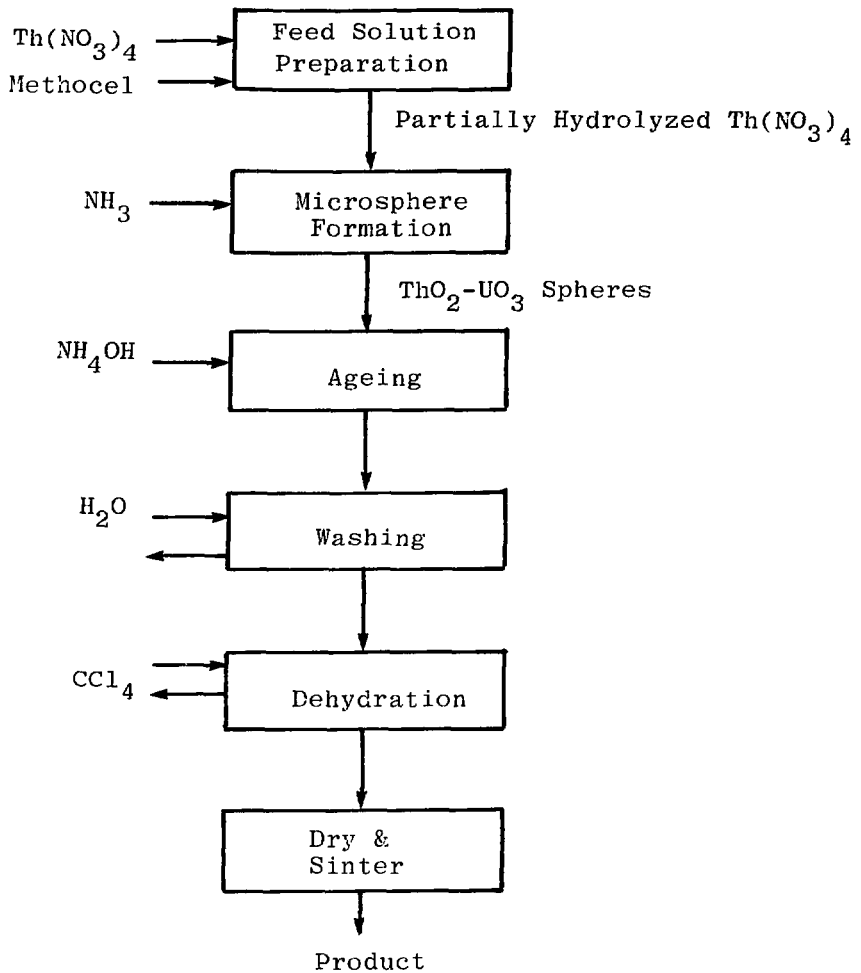
FIGURE 12: PROCESS FLOW SHEET FOR PREPARATION OF $(Th,U)O_2$ MICROSPHERES VIA THE GEL-SUPPORTED PRECIPITATION PROCESS.

The solvent-extraction process is attractive because the technology is a logical extension of the reprocessing techniques; it is readily adapted to continuous production and it is probably the fastest technique for making spheres. Also, a considerable amount of pilot plant experience has been accumulated in the United States and Italy. ORNL has demonstrated the viability of the solvent-extraction technique with a near continuous engineering demonstration to produce $(Th,U)O_2$ spheres[32]. The C.N.E.N. process has been used to produce fine $(U,Pu)O_2$ spheres on a semicontinuous basis[33]. Two possible drawbacks to solvent extraction are: (1) it is difficult to extract all the nitrate from solution so the final sphere density might be too low, (2) the process does not yield concentrated sols, so large spheres are difficult and extrudable clays are not possible.

Although the precipitation-peptization method is the oldest sol-gel technique, it seems too messy for remote operation because the thorium hydroxide precipitate is awkward to handle. Nevertheless, more recent modifications to the basic process seem to work. For example, Interfuel in Belgium is using the KEMA U(VI) process to fabricate $(U,PU)O_2$ spherepac fuel and they report good results[34].

The gel-supported precipitation technique seems to be the simplest sol-gel method since the denitration and sol preparation steps are avoided. The sphere-forming step is reliable and the recycling of organic solvents is avoided. Pilot plants using the SNAM process are operating or planned in the United Kingdom, West Germany and Italy. The process does generate large volumes of waste which must be neutralized. Ageing, washing and drying are slow and the spheres must be sintered at $\sim 1400°C$ to achieve high density. Nevertheless, the process does have considerable appeal.

Currently WNRE has adopted the denitration-peptization technique, to produce sols for extrusion and spherepac fuels, for several reasons. Firstly, the process is readily adapted to a lab-scale operation for

fabricating experimental fuel for irradiations. Secondly, the ORNL work is by far the best-documented and ORNL has had the most experience in a remote pilot plant. Thirdly, it is the only process known to produce concentrated clays for extrusion. Although the denitration step seems awkward, it can be done outside the remote facility since ^{233}U is not introduced until later in the process. Most of the experience has been with spheres in the 300 to 500 μm size range, and fabrication of smaller and larger spheres may be difficult using this process.

REFERENCES

1.   S.R. Hatcher, "Fuel for Nuclear Power in Canada: Options
        Beyond the Year 2000", Can. Business Review, 2 (4) (1975).

2.   E.D. Arnold, "Radiation Hazards of Recycled ^{233}U Thorium
        Fuels", Nuclear Safety, 5, 382 (1964).

3.   R.K. McGeary, "Mechanical Packing of Spherical Particles", J.
        Am. Ceram. Soc. 44, 513 (1961).

4.   J.E. Ayer and F.E. Soppet, "Vibratory Compaction: I, Com-
        paction of Spherical Shapes", J. Am. Ceram. Soc. 48, 180
        (1965).

5.   M.D. Freshley, "A Comparison of Pellet and Vipac Nuclear
        Fuels", Nuclear Engineering and Design, 21, 264 (1972).

6.   M.J. Kelly, "An Analytical Approach to Waterlogging Failure",
        Oak Ridge National Laboratory Report, ORNL-3867 (1966).

7.   M.K. Millhollen, G.R. Horn and J.L. Bates, "Hydriding in
        Purposely Defected, Zircaloy-Clad Fuel Rods", Hanford Report,
        HW-65465 (1961).

8.   G.H. Chalder, "Irradiation Behaviour of Extruded UO_2", Atomic
        Energy of Canada Limited Report, AECL-1990 (1964).

9.   R.W. Jones and J.L. Crosthwaite, "Uranium Carbide Fuel for
        Organic Cooled Reactors", Atomic Energy of Canada Limited
        Report, AECL-4443 (1973).

10.   J. Veeder, "Thermo-Elastic Expansion of Finite Cylinders",
        Atomic Energy of Canada Limited Report, AECL-2660 (1967).

11.   T.J. Carter, "The Effects of UO_2 Pellet Shape on Strains
        Induced in Collapsible Zircaloy Cladding-Status May 1976",
        Atomic Energy of Canada Limited Report, AECL-5978 (1977).

12.   P.J. Anderson, "The Ion Absorption Properties of Thoria",
        Trans. Faraday Soc. 54, 130 (1958).

13.   H.W. Douglas and J. Burden, "The Surface Charge and Sedimenta-
        tion of Thoria Suspensions", Trans. Faraday Soc. 55, 350
        (1959).

14.   R.G. Sowden, K.E. Francis and B.R. Harder, "Surface Electrical Studies of Thoria and Plutonia Suspensions", Nucl. Sci. Eng. 16, 1 (1963).

15.   D.H. Napper, "Colloid Stability", Ind. Eng. Chem. Prod. Res. Develop. 9, 467 (1970).

16.   I.L. Thomas and K.H. McCorkle, "Theory of Oriented Flocculation", J. Colloid and Interface Sci. 36, 110 (1971).

17.   K.H. McCorkle, "Surface Chemistry and Viscosity of Thoria Sols", Oak Ridge National Laboratory Report, ORNL-TM-1536 (1966).

18.   F.A. Olson, R.K. Chang, C.S. Olsen and M.E. Wadsworth, "A Model for Shrinkage of Thoria Gel Based on Kinetics and Surface Characterization Using Infrared Spectroscopy", Symposium on Sol-Gel Processes and Reactor Fuel Cycles, Gatlinburg, Tennessee, May 4-7, 1970, p. 476, CONF-700502.

19.   E. Sturch, "A Study of the Viscosity of Thoria Sols", Oak Ridge National Laboratory Report, ORNL-TM-258 (1962).

20.   J.P. McBride, "Laboratory Studies of Sol-Gel Processes at the Oak Ridge National Laboratory", in "I Processi Sol-Gel per la Produzione di Combustibili Ceramici", proceedings of Symposium on Sol-Gel Processes for the Production of Ceramic Nuclear Fuels, held in Turin, Italy, 1967. Comitato Nationale Energia Nucleare, Rome, 1968. p. 161.

21.   D.E. Ferguson, in Progress in Nuclear Energy, Series III, Process Chemistry, Pergamon Press, Oxford and New York, 1970. p. 37.

22.   M.J. Bannister, "Sintering Mechanisms in Thoria Gel", J. Am. Ceram. Soc. 58, 10 (1975).

23.   C.S. Morgan, K.H. McCorkle and G.L. Powell, "Pore Growth in Sintered Thoria", J. Am. Ceram. Soc. 59, 104 (1976).

24.   P.A. Haas, "Process Requirements for Preparing ThO_2 Spheres by the ORNL Sol-Gel Process", Oak Ridge National Laboratory Report, ORNL-TM-3978 (1972).

25.   C.C. Haws, J.L. Matherne, F.W. Miles and J.E. Van Cleve, "Summary of the Kilorod Project", Oak Ridge National Laboratory Report, ORNL-3681 (1965).

26.   P.A. Haas, "Sol-Gel Preparation of Spheres: Design and Oper-
        ation of Fluidized Bed Columns", Oak Ridge National Laboratory
        Report, ORNL-4398 (1969).

27.   R.B. Fitts, H.G. Moore, A.R. Olsen and J.D. Sease, "Sol-Gel
        Thoria Extrusion", Oak Ridge National Laboratory Report, ORNL-
        4311 (1968).

28.   J.G. Moore, "A Sol-Gel Process for Preparation of ThO_2-UO_3
        Sols from Nitrate Solutions by Solvent Extraction with Amines",
        Oak Ridge National Laboratory Report, ORNL-4095 (1967).

29.   G. Cogliati, F. Collenza, R. Lanz, V. Lupparelli, P. Maltzeff,
        E. Mezi and A. Recrosio, "Sol-Gel Processes for the Production
        of Ceramic Fuels at C.N.E.N. Laboratories", in "I Processi
        Sol-Gel per la Produzione di Combustibili Ceramici", proceed-
        ings of Symposium on Sol-Gel Processes for the Production of
        Ceramic Nuclear Fuels, held in Turin, Italy, 1967. Comitato
        Nationale Energia Nucleare, Rome, 1968. p. 241.

30.   M.E.A. Hermans and H.S.G. Slooten, "Preparation of UO_2 and
        ThO_2 Powders in the Subsieve Range", Proceedings of the Third
        International Conference on the Peaceful Uses of Atomic Energy,
        31 August-9 September, 1964, United Nations Publication, New
        York, 1965. Volume II, p. 450, A/CONF. 28/p/634.

31.   P. Brambilla, P. Gerontopulos, A.G. Facchini, D. Neri, "The
        SNAM Process for the Production of Ceramic Nuclear Fuel Micro-
        spheres", Symposium on Sol-Gel Processes and Reactor Fuel Cycles",
        Gatlinburg, Tennessee, May 4-7, 1970. p. 191, CONF-700502.

32.   R.G. Wymer, "Sol-Gel Processes at Oak Ridge National Laboratory",
        Proceedings on Sol-Gel Processes for Fuel Fabrication, Vienna
        1973, p. 129, IAEA-161 (1974).

33.   G. Cogliati and A. Facchini, "A Pilot Plant for Continuous
        Preparation of U-Pu Oxide Spheres", Symposium on Sol-Gel
        Processes and Reactor Fuel Cycles, Gatlinburg, Tennessee,
        May 4-7, 1970. p. 210, CONF-700502.

34.   P.F. Sens, J.B.W. Kanij, K.A. Nater and J.H.N. Verheugen,
        "Fabrication of Vibrasol Fuel Rods", Proceedings of the First
        European Nuclear Conference, Paris, April 1975. Progress in
        Nuclear Energy Series, Nuclear Energy Maturity, Pergamon
        Press, Oxford and New York, 1976. Volume 7, p. 13.