

**Keywords: Metal hydrides, Sol-gel, External gelation**

**Development of a Fabrication Process for  
Sol-Gel / Metal Hydride Composite Granules (U)**

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Metal Hydrides, Sol-gel,  
Fabrication process

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Sol-Gel / Metal Hydride Composite Granules (U)**

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**1.0 EXECUTIVE SUMMARY**

An external gelation process was developed to produce spherical granules that contain metal hydride particles in a sol-gel matrix. Dimensionally stable granules containing metal hydrides are needed for applications such as hydrogen separation and hydrogen purification that require columns containing metal hydrides. Gasses must readily flow through the metal hydride beds in the columns.

Metal hydrides reversibly absorb and desorb hydrogen and hydrogen isotopes. This is accompanied by significant volume changes that cause the metal hydride to break apart or decrepitate. Repeated cycling results in very fine metal hydride particles that are difficult to handle and contain. Fine particles tend to settle and pack making it more difficult to flow gases through a metal hydride bed. Furthermore, the metal hydrides can exert a significant force on the containment vessel as they expand.

These problems associated with metal hydrides can be eliminated with the granulation process described in this report. Small agglomerates of metal hydride particles and abietic acid (a pore former) were produced and dispersed in a colloidal silica / water suspension to form the feed slurry. Fumed silica was added to increase the viscosity of the feed slurry which helped to keep the agglomerates in suspension.

Drops of the feed slurry were injected into a 27-foot tall column of hot (~70°C), medium viscosity (~3000 centistokes) silicone oil. Water was slowly evaporated from the drops as they settled. The drops gelled and eventually solidified to form spherical granules. This process is referred to as external gelation. Testing was completed to optimize the design of the column, the feed system, the feed slurry composition, and the operating parameters of the column. The critical process parameters can be controlled resulting in a reproducible fabrication technique.

The residual silicone oil on the surface of the granules was removed by washing in mineral spirits. The granules were dried in air at 40°C. The granules were heated to 230°C for 30 minutes in argon to remove the remaining water and organic materials.

The resulting product was spherical composite granules (100 to 2000 micron diameter) with a porous silica matrix containing small agglomerates of metal hydride particles. Open porosity in the silica matrix allows hydrogen to permeate rapidly through the matrix but the pores are small enough to contain the metal hydride particles. Additional porosity around the metal hydride particles, induced using abietic acid as a pore former, allows the particles to freely expand and contract without fracturing the brittle sol-gel matrix.

It was demonstrated that the granules readily absorb and desorb hydrogen while remaining integral and dimensionally stable. Microcracking was observed after the granules were cycled in hydrogen five times. The strength of the granules was improved by coating them with a thin layer of a micro-porous polymer sol-gel that would allow hydrogen to freely pass through the coating but would filter out metal hydride poisons such as water and carbon monoxide. It was demonstrated that if a thin sol-gel coating was applied after the granules were cycled, the coating not only improved the strength of the granules but the coated granules retained their strength after additional hydrogen cycling tests. This additional strength is needed to extend the lifetime of the granules and to survive the compressive load in a large column of granules.

Additional hydrogen adsorption tests are planned to evaluate the performance of coated granules after one hundred cycles. Tests will also be performed to determine the effects of metal hydride poisons on the granules. The results of these tests will be documented in a separate report.

The process that was developed to form these granules could be scaled to a production process. The process to form granules from a mixture of metal hydride particles and pore former such as abietic acid can be scaled up using commercial granulators. The current laboratory-scale external gelation column produces approximately one gram of granules per hour. To increase the production output from a single column, multiple feed injection systems in a larger diameter column could be used.

## **2.0 INTRODUCTION**

Hydrogen absorbing materials have many applications including hydrogen storage, gettering, and purification. Materials that have different absorption and desorption rates for the hydrogen isotopes can be used for isotope separations.

Various metals and metal alloys can reversibly absorb and desorb large quantities of hydrogen and hydrogen isotopes. A metal hydride is formed when hydrogen is absorbed, however, the entire category of metals and alloys that are capable of forming metal hydrides, even if they have not absorbed hydrogen, are often referred to as metal

hydrides. A large volume change occurs when the metal hydride forms. The hydride form of the material is usually much more brittle than the metal itself. Cycling of the material in hydrogen creates internal stresses that are sufficient to cause cracking. Many applications require thousands of cycles. Brittle metal hydrides eventually break down into very small particles. This size reduction of the material is referred to as decrepitation.

Although the fine particles are still effective at absorbing and desorbing hydrogen, the fines cause problems in some of the applications for metal hydrides. For example, as a bed of metal hydride materials decrepitate, the formation of fines restricts the ability of gas to readily flow through the bed. This is major problem in separating hydrogen from low concentration gas streams or in hydrogen purification.

In some applications the filters used to contain the metal hydrides are easily clogged by fine particles. Metal hydride applications at the Savannah River Site (SRS) usually involve hydrogen isotopes such as tritium. Since tritium is a hazardous material, the formation of fine particles containing tritium presents a significant safety concern because the fines are more easily dispersed and are difficult to contain. As a bed of metal hydride particles absorbs hydrogen and expands, the stresses on the walls of the vessel are also a concern.

### 3.0 BACKGROUND

The decrepitation of metal hydrides has been recognized as a problem for several years. One solution to this problem is to disperse the metal hydride in a matrix. The matrix must be porous enough to allow rapid hydrogen permeation; however, the pores must be small enough to contain the fine metal hydride particles. In addition, the matrix must be able to withstand the stresses created by the expansion and contraction of the metal hydride. For many applications, the preferred form of the composite is small pellets or granules that are free-flowing and strong enough to be easily handled. The composite should be able to withstand thousands of cycles without significant damage.

Several attempts have been made to develop particulate composites to contain metal hydrides. The compositions for some of these composites have been disclosed in U.S. patents. Matrix materials that have been used for metal hydride composites include polymers,<sup>1,2</sup> metals,<sup>3</sup> and glass.<sup>4,5,6</sup> Each of these patents offers a unique solution to the challenge of producing a dimensionally stable metal hydride composite. However, there is still a need for a metal hydride composite that can be produced by a commercially viable process.

Several commercial granulation processes were considered as methods to produce kilogram quantities of metal hydride composites. Many of these processes produce granules that are basically low-density agglomerates of fine particles. For some applications the granules could be densified and strengthened by sintering, however, the high temperatures required for sintering would degrade metal hydrides. Similarly,

granulation processes such as spray drying require relatively high operating temperatures to produce dense granules. The spray drying temperatures would be sufficient to degrade the metal hydride. Therefore, the granulation process must be able to produce high strength granules without relying on a high temperature heat treatment. Freeze granulation and external gelation were considered as viable processes to produce metal hydride granules.

Freeze granulation is a two-step process. A liquid or slurry can be sprayed into liquid nitrogen and frozen as small granules. The frozen granules are then slowly freeze dried. Granules with a fairly uniform size can be produced by freeze granulation.<sup>7</sup> Equipment is commercially available to perform the freeze granulation process.<sup>8</sup>

Freeze granulation offers the potential of forming granules at low temperatures that will not affect the ability of the metal hydride particles to absorb hydrogen. It must be demonstrated that granules with the required strength and microstructure to contain metal hydride particles can be produced by this process.

External gelation is basically a controlled drying process in which a suspension is injected into a column of hot silicone oil. Droplets of the suspension are slowly dried in the hot oil as they settle. Relatively dense, spherical granules can be produced by external gelation. The oil temperatures required for external gelation of aqueous slurries are not high enough to degrade the metal hydride. Gelation processes have found commercial applications in the production of nuclear fuel.<sup>9</sup>

The selection of a matrix material is also critical. Heung et. al.<sup>4</sup> have demonstrated that a porous glass matrix produced by sol-gel techniques is effective at containing fine metal hydride particles while allowing the rapid permeation of hydrogen gas. The quartz matrix produced by sol-gel techniques includes very high volumes of continuous porosity. Standard sol-gel processing techniques are very tedious, expensive, and difficult to reproduce.

It is not realistic for a very porous, brittle matrix such as that created by sol-gel processing to withstand the stresses created by the large volume changes typically associated with cycling metal hydrides. Several approaches have the potential to reduce or eliminate the cracking problems associated with metal hydride composites.

One approach is to obtain enough ductility in the matrix so that the expansion of the metal hydride would not cause cracking. It has been shown that silicate materials can be organically modified to exhibit some ductility<sup>10,11</sup> but it was considered unlikely that these materials would have enough ductility to accommodate the strains resulting from the expansion of metal hydride particles.

Another approach<sup>3</sup> had demonstrated that, if porosity could be induced around the metal hydride particles, a dimensionally stable composite could be produced. Substances such as salts or organic materials can be mixed with metal hydride particles. Small agglomerates of this mixture can be dispersed in the matrix during the fabrication



process. If the additive can be removed using a low temperature heat treatment that does not degrade the metal hydride or matrix materials, the final composite will consist of clusters of metal hydride particles in voids dispersed throughout the matrix. Since the metal hydride particles are not in intimate contact with the matrix, no stresses will be transferred to the matrix as the composite is cycled in hydrogen. The utilization of a pore former has been demonstrated to produce dimensionally stable metal hydride composites<sup>3</sup> and could be implemented in conjunction with the external process.

## 4.0 PROCESS DEVELOPMENT

The process development work was performed at the Clemson Environmental Technologies Laboratory (CETL) at Clemson University. The research at Clemson was funded with a subcontract<sup>12</sup> through the South Carolina Universities Research and Educational Foundation (SCUREF). The Hydrogen Technology Section (HTS) performed the hydrogen absorption /desorption tests. The composite granules were characterized before and after the hydrogen cycling tests using an optical stereomicroscope. Some of the granules were also characterized using the scanning electron microscope (SEM) operated by the Analytical Development Section (ADS).

Since the results of these studies will not directly impact plant operations, the experiments were considered as scoping activities. Weights were obtained with calibrated balances. Experimental data were recorded in laboratory notebooks.

The ultimate objective of this research was to develop a process to produce dimensionally stable sol-gel / metal hydride composite granules. In order to ensure that the process could be reproduced, it was important to be able to precisely control the critical parameters and to understand their effects on the characteristics of the granules. The process development activities included matrix composition selection, granulation process selection, process demonstration, critical process parameter determination, product testing, and process optimization.

### 4.1 Composition

The first step in the process development required the selection of a matrix material and metal hydride particles with the desired morphologies.

**4.1.1 Matrix:** Colloidal silica (14 nanometer) was selected as the matrix material. This was purchased in the solid form as fumed silica and in a water-based suspension that contained 40 wt.% silica. Fumed silica was available in other size ranges and suspensions were available in other concentrations but none of these were evaluated in this study.

**4.1.2 Metal Hydride:** A lanthanum-nickel-aluminum alloy (LANA<sub>0.75</sub>) was selected for use in these tests since it was readily available and its properties are well-established. It is expected that other metal hydride materials could be substituted with similar results.

In order to minimize localized stresses associated with the expansion of the metal hydride particles, a uniform dispersion of very fine metal hydride particles was desired. Tests were performed to determine if this could be achieved by milling the metal hydride particles. Metal hydride granules were ball-milled in a porcelain jar with 10 mm spherical zirconia grinding media for 24 hours. Tests were performed in ethanol and in water. The particle size was reduced to <5 microns as desired but the metal hydride oxidized during the milling process and would not absorb hydrogen. A milling process for metal hydrides could be developed if sufficient funding was available to set up a mill in a high purity inert atmosphere or in a hydrogen atmosphere. This has already been done commercially. The Materials Technology Section is currently establishing the capability to grind and mix metal hydride powders in a high energy mill under a controlled atmosphere.

Since milling was not successfully demonstrated, all testing described in this report was performed using metal hydride particles that had been formed by the decrepitation of granules using multiple hydrogen absorption / desorption cycles. The decrepitated particles were slowly exposed to oxygen. This technique oxidized only the surface of the metal hydrides and did not adversely affect their ability to absorb hydrogen. The metal hydride particles were screened to <20 microns for all of the tests described in this report.

## 4.2 Process Selection

Based on a survey of the literature it was determined that the external gelation and freeze granulation processes would be capable of forming composite granules without affecting the ability of metal alloys to absorb hydrogen. Preliminary experimental tests were performed to provide a basis for selecting a granulation process.

**4.2.1 Freeze Granulation:** Freeze granulation was evaluated by submitting a suspension to a commercial vendor for a granulation test. The suspension sent to the vendor contained 20 wt.% metal hydride particles in 40 wt.% colloidal silica in water.

The freeze-granulated feed was analyzed using the scanning electron microscope (SEM). The size of the granules ranged from a few microns to nearly one millimeter (Figure 1). Many of the granules were actually aggregates of smaller granules. As shown in Figure 2, the granules had large, open pores. The metal hydride particles appeared to be evenly dispersed in the silica matrix. The granules were very fragile and easily crushed during handling. The vendor was confident that freeze granulation process could be optimized to produce a more uniform size distribution of granules but the process typically produces porous, fragile granules.

Since, the density and strength of the freeze granulated material was very low, dip coating in a tetraethyl orthosilicate (TEOS) based solution was performed in an attempt to fill the porosity and strengthen the granules. The composition of the coating solution is shown below:

130g water  
40g ethanol  
30g TEOS  
0.2 g Murratic acid (31.45% HCl)

The freeze granulated material was sieved to >425 microns and dip coated, in separate tests, for a period of 5 minutes, 1 hour, and one week. The SEM was used to characterize the coated granules. As shown in Figure 3, the one-hour dip coating was at least partially successful in filling the large pores, but the coating was not continuous and was badly cracked on some granules. A 5-minute dip coating had little effect on the strength of the granules. Granules that were dip coated for one week in the TEOS based solution still had some large open porosity.

No hydrogen cycling tests were performed on the freeze granulated material since the metal hydride feed had been oxidized during milling. The freeze granulated material appeared very fragile and unlikely to contain decrepitated metal hydride particles because of the large open porosity. It may be possible to modify the parameters of the freeze granulation process to produce denser and stronger granules or to develop coatings to fill the voids.

**4.2.2 External Gelation:** The initial tests of the external gelation process involved using a pipette to drip aqueous slurries containing colloidal silica and metal hydride particles into a burette full of hot silicone oil to determine if granules could be formed. A few granules were fabricated but there was not enough material produced in these preliminary tests to evaluate in hydrogen cycling tests. The granules were characterized with a scanning electron microscope. As shown in Figures 4 and 5, spherical granules with the desired microstructure could be produced. The original tests were performed at relatively high temperatures (>95°C) resulting in the “blow-out” type flaws prevalent in the granules shown in Figure 4.

It was realized that the column height, oil viscosity, drop size, and oil temperature were critical process variables that could easily be controlled and reproduced. It appeared likely that most of the defects observed in the granules from the preliminary tests could be eliminated by adjusting these process variables to decrease the drying rate. External gelation was selected as the most promising granulation process since the granules appeared to be much stronger than those produced by freeze granulation. In addition, it appeared that the porosity in the freeze granulated material was too large to contain the metal hydride particles. Therefore, the remainder of the experimental program focused on developing an external gelation process.

### 4.3 Development of the External Gelation Process

The basic design of the column was based on previous work that had been performed at the Oak Ridge National Laboratory.<sup>9</sup> The feed system requirements and the dimensions of the column were dependent on the composition of the feed slurry and on the process

parameters. The design of the feed system and column evolved as the process parameters were optimized.

**4.3.1 Feed Slurry:** The composition of the feed slurry was a critical parameter. A few tests with an ethanol-based suspension were performed. Because of the high vapor pressure of the ethanol, the drops could be solidified much more rapidly and at lower temperatures than water-based suspensions. However, the resulting granules, shown in Figure 6, were very fragile and work with ethanol-based suspensions was discontinued.

The flowsheet and remaining results are all based on the external gelation of water-based suspensions. The feed slurry contained various concentrations of metal hydride particles dispersed in 40-wt.% colloidal silica in water. A high solids content was desired to reduce the amount of water that had to be evaporated. It was postulated that this would minimize the shrinkage and the associated stresses as the slurry gelled and solidified. It was found that small additions of fumed silica to the slurry increased the viscosity enough to minimize settling of the metal hydride agglomerates within the droplet before gelation occurred.

**4.3.2 Feed System:** The first step in developing an apparatus to perform external gelation required the development and testing of a feed system. The process required a method to continuously drip a suspension of metal hydride particles and colloidal silica into the oil at the top of column.

A micro-peristaltic pump was selected to pump the feed suspension through a small orifice and into the silicone oil. The feed tube size, velocity of incoming oil, and feed pump speed could be controlled to produce the desired frequency of drop formation. The feed parameters were also dependent on the viscosity of the feed slurry. Adjusting the speed of the micro-peristaltic and/or changing the size of the tubing controlled the feed rate. The feed rate controlled the production rate of granules in the column. A photograph of the peristaltic pump feed system is shown in Figure 7.

An attempt to use air pressure in place of the peristaltic pump to feed the slurry into the column was unsuccessful. A closed glass vessel with feed-through ports for the air and slurry was designed and fabricated. This low pressure feed system is shown in Figure 8. An ultra-low pressure regulator was installed to maintain a more constant pressure but a constant feed rate could not be maintained with this system. Apparently, the pressure required to maintain the feed rate varied as the slurry plugged or gelled in the feed line.

Small drops were preferred since they settled more slowly. This minimized the height needed to dry the granules in the column. Testing indicated that the orifice size of the slurry feed tube could be decreased to produce slightly smaller drops but surface tension caused the drops to stick to the orifice and grow until gravity overcame the surface tension. This limited the ability of the feed system to produce small drops. It was found that smaller drops could be produced by feeding the slurry into the incoming stream of silicone oil. The oil pulled the droplets from the feed tube orifice. Various feed system designs utilizing this principle were evaluated. It was demonstrated that the feed slurry

could be injected through a small orifice in the side of the oil feed tube or into the oil stream just as it exited the column. It was also shown that the droplet size could be reduced by decreasing the inner diameter of the oil feed tube enough to increase the velocity of the oil flowing through the tube. The final design also considered ease of installation, removal, and cleaning.

Initially, the goal was to design a feed system that would produce uniformly sized drops. In order to produce uniform sized granules, the drops had to be spaced far enough apart to minimize the probability of the droplets colliding as they settled in the column of silicone oil. In the liquid phase, collisions caused the droplets to combine to form larger drops that settled faster and required longer drying times. During the gelation phase, collisions caused the droplets to stick together to form agglomerates that settled more rapidly than single drops. As shown in Figure 9, fairly-uniformly sized granules (500 to 900 microns) could be produced if the drip rate was slow enough to eliminate collisions and coalescence of drops in the column. A fairly uniform drop size was also considered advantageous in designing a column and establishing operating conditions that would solidify all of the drops by the time they settled to the bottom of the column. With all of the drops about the same size, their settling rate and drying time were nearly equivalent. A steady drip rate of ~100 drops per minute was achieved using 0.89 mm ID flexible tubing in a micro-peristaltic pump with a setting of 70 microliters/minute.

As testing progressed, it was realized that the packing density of the granules could be improved by producing granules with a larger size distribution. This would increase the effective metal hydride concentration in a processing vessel. By decreasing the diameter of the oil feed tube from  $\frac{3}{8}$ " to  $\frac{1}{4}$ ", the velocity of the oil was increased sufficiently to break the feed slurry into a nearly continuous stream of very small (<100 microns) droplets. Many of these small drops coalesced while still in the liquid state. This produced a wide size range of granules with a few granules as large as 2 mm. The column design and operating parameters were adjusted to solidify the largest size granules. Based on a sieve analysis of a typical batch of granules, approximately 50 wt.% of the granules were larger than 850 microns and about 12 wt.% were less than 425 microns. The size distribution of the granules was heavily dependent on the slurry feed rate. A digitally controlled peristaltic pump was required to reproduce the feed rate.

**4.3.3 Column:** A vertical column contained the silicone oil for the external gelation process. The top section of the column consisted of two concentric tubes. The feed system described above injected drops of the metal hydride / colloidal silica suspension into the center tube at the top of the column. There was an overflow port near the top of the outer tube and a vent port just above the overflow port. The feed suspension was injected into the inner tube to prevent the droplets from being discharged through the overflow port.

The height of the columns for the external gelation tests were modified as the optimum process parameters were defined. The height of the column was determined by the settling time required for the largest drops to solidify in the column to the point at which coalescence and agglomeration were no longer a concern. The time required to dry the

drops was dependent on the composition of the feed suspension, the droplet size, and the temperature of the silicone oil. The height of the column, droplet size, and the viscosity of the silicone oil controlled the settling time in the column.

The original column was only 8 feet tall and fabricated from clear, 2-inch diameter PVC. The oil viscosity of 50 centistokes did not result in sufficient settling time in this column. It was very important for the droplets to be solidified before entering the bottom transition section of the PVC column. There was enough turbulence in the column of oil that the drops seldom fell straight down the center of the column. The drops became very sticky as they gelled and would sometimes stick to the walls of the column. In the early tests, some of the drops stuck in the transition section which became a problem because drops tended to accumulate and eventually plug the transition to the tube.

Contacts between the drops became more frequent in the coiled tube. Drops that were still in the liquid phase would combine to form larger drops. These drops often became too large to solidify as they passed through the coil. Drops that were still in the gel-state formed large agglomerates as they collided. These larger drops and agglomerates moved through the tube faster than the small droplets. The larger drops or agglomerates usually consumed the smaller drops before they were discharged from the column.

Tests were performed in which the oil viscosity was increased to 500 centistokes. Most of the granules could be solidified when the silicone oil in the column was heated to nearly the boiling point of water. However, the high temperatures caused very rapid drying rates and ruptured many of the granules. The high operating temperature also caused the clear PVC to become very cloudy.

When it was determined that a lower operating temperature was needed, the height of the column was increased to compensate for the slower drying rate. A few tests were performed using a 16-foot tall column constructed from a steel pipe. Although the gelation process could not be observed in the steel pipe, the tests were useful in determining the optimum column height and oil viscosity.

Glass was ultimately used to fabricate the column and the oil viscosity was increased to 3000 CTS. The tendency for drops to stick on the sidewalls was eliminated with the glass column. Six 3-foot sections of 4-inch diameter glass tubes were coupled together with o-ring seals and clamps to form the 18-foot tall column shown in Figure 10. The bottom section of the glass column was slowly tapered from a 4-inch diameter to a 1/4" ID orifice.

The 18-foot tall glass column was relocated and three additional 3-foot sections were later added to increase the height of the column to 27 feet. This increased column height improved the flexibility to allow testing at lower temperatures and with larger droplets. The column was supported by vertical steel Unistrut<sup>®</sup> mounted between the levels of a high bay facility at the CETL as shown in Figures 11,12, and 13. The feed system and the top sections of the column were accessed from the third level platform and the bottom of the column was accessed from the bottom level of the facility. A plumb-bob down the

center of the column was used to set the vertical orientation. The entire column was heated externally by two separate coils of heat tape. The temperature of the heat tape was thermostatically controlled for each heating zone. Initially, digital thermometers were inserted through ports at four locations in the column to monitor the oil temperature. The thermometers were replaced with thermocouples that read directly to a computer. The column was insulated but portions of the insulation could be removed to view the granules as they settled. A large galvanized steel catch pan was located below the column in case of a spill.

**4.3.4 Coil:** The silicone oil and granules in the column discharged through the tapered bottom section of the column into a coiled  $\frac{3}{8}$ " OD Tygon<sup>®</sup> tube. The tube had an open-ended discharge into an oil bath where the granules were collected. The oil discharge rate from the column was controlled by the size of the tube (ID and length) as well as the process conditions (oil viscosity and temperature). The tubing was coiled around a 4" diameter steel pipe. In the initial set-up, 100 feet of tubing was coiled onto a four foot long pipe but it was difficult to maintain a continuous downward orientation to prevent hold-up of the granules in the line. The length of the tubing was reduced to 30 feet and finally to 15 feet to eliminate this problem and to balance the discharge rate with the desired flow rate of the incoming oil. The entire tube discharge line was heated to 65°C with self-regulating heat-tape that was wrapped around the steel pipe and below the tubing. Insulation was inserted into the steel tube and around the coil of polyethylene tubing.

**4.3.5 Granule Collection:** The granules were discharged from the coil in a stream of silicone oil. The granules were collected onto a 200 mesh (75 micron) sieve in an oil bath. The temperature of the oil in the bath was thermostatically controlled at 82°C. Granules were collected in the sieve within the hot oil to further dry the granules. The granule collection system is shown in Figure 14. The granules were aged in the warm oil overnight and cleaned the following day.

**4.3.6 Oil Recirculating System:** The viscosity of the silicone oil in the column was a major factor in controlling the settling rate of the drops. A slow settling rate was desired to minimize the height of the column required to solidify the feed suspension drops. The maximum viscosity of the oil that could be used in the column was at first limited by the ability of a peristaltic pump to recirculate the oil to the top of the column. The peristaltic pump was replaced with a diaphragm metering pump. The oil was discharged into an oil bath and reheated to 82°C to lower its viscosity and make it easier to recirculate. The  $\frac{3}{8}$ " copper return-line for the oil was run between the column heat tape and insulation to help maintain its temperature.

A second constant temperature oil bath was used to control the temperature of the incoming oil. The recirculated oil passed through a copper coil that was submersed in the oil bath just prior to reentering the column and the temperature of the incoming oil was measured with a thermocouple inserted into the oil feed tube. The temperature of the incoming oil was a critical process variable. The feed slurry was injected into the incoming oil stream. It was found that if the temperature of the incoming oil was at least

10°C lower than that of the oil in the column, the entrained drops of feed slurry would be carried down into the column with the incoming stream as it rapidly sank into the higher temperature oil. If the temperature of the incoming oil was too close to that of the column oil, the drops floated on the surface of the oil and coalesced.

Silicone oil was commercially available in a wide variety of viscosities and could be blended to an intermediate viscosity as required. The oils were blended in a 20-gallon stainless steel vessel with a pneumatic-powered impeller mixer using a 6-inch diameter blade. This apparatus is shown in Figure 15. Self-regulating heat tape (65°C) was wrapped around the mixing vessel to heat the oil. This lowered the viscosity of the oil and made it easier to blend and transfer from the vessel. The viscosity of the silicone oil decreased as the temperature increased. Silicone oils with viscosities ranging from 50 to 5000 CTS (centistokes) were used in these tests. All of the tests in the glass column were performed using silicone oil with a viscosity of 3000 CTS. This viscosity represented a good compromise between flowability and settling rate.

The height of the overflow port dictated the oil level in the column. Oil from the overflow port at the top of the column was discharged to the oil bath at the base of the column. The oil was pumped into the top of the column at a rate only slightly greater than the discharge rate. Once the pump speed was adjusted to the proper rate, no further adjustments were required to maintain the oil level in the column. There was also a drain port near the bottom of the column.

**4.3.7 Process Parameters:** The process development objectives included optimization of the critical parameters. A wide range of process parameters were evaluated in these studies. Critical parameters such as oil viscosity, oil temperature, and feed rate were optimized through a series of tests over a wide range of conditions. In addition, the interrelationship of these parameters and their effects on the characteristics of the granules were determined.

These experiments were not performed as a statistically designed parametric study, but rather as a series of tests in which gradual improvements were made in the column design, feed composition, and process parameters. In many cases, relatively small batches of material were processed to evaluate changes in the column design or process parameters. The goal of these preliminary tests was often to establish conditions that would gel and solidify the granules in the column after modifications had been made to the feed system or column design. The granules produced in these preliminary tests were observed with a stereomicroscope but were not tested in hydrogen. More controlled experiments that included hydrogen testing were used to optimize the feed composition. In these experiments the metal hydride content was incrementally increased starting from 20 wt.%. Similar incremental testing was performed to determine the optimum concentration of the pore former.

No attempt will be made to describe each experiment that was performed as part of this process development; however, the range of test conditions is presented in Table 1. In addition to the conditions reported in Table 1, experiments were performed with various



sized tubes to feed the slurry as well as various feed rates. The optimum size slurry feed tube had an inner diameter of 0.0425 inch and an outer diameter of 0.0625 inch. The oil flow rate into the column was also adjusted to balance the oil discharge rate from the coil. The oil discharge rate varied as the coil length was changed, as the oil viscosities changed, and as the column height changed. The coil temperature was maintained at 65°C for all of the runs. The test conditions were held constant for column runs that produced granules for hydrogen testing. However, in many of the preliminary test runs the process conditions were adjusted during the run.

The temperature of the silicone oil in the column controlled the drying rate of the drops. High temperatures were obviously preferred to maximize the drying rate; however the maximum temperature of the silicone oil had to be limited to prevent water from evaporating too quickly from the droplets. At oil temperature above 95°C very rapid evaporation rates caused some of the drops to burst in the oil. At oil temperatures above 80°C some of the granules appeared to have formed a shell in which rapid evaporation caused the liquid interior to pressurize the shell. This resulted in spherical granules with a hole in the shell as shown in Figure 4.

**4.3.8 Granule Cleaning:** The granules were collected onto a 200-mesh sieve and aged in warm silicone oil overnight prior to cleaning. In the original tests the silicone oil was removed from the granules by washing in hexane. A peristaltic pump was used to recirculate hexane through the bed of granules on the sieve. The hexane was then removed by washing with ethanol using the pump to recirculate the ethanol through the bed of granules on the sieve. The ethanol was evaporated by drying in air at 40°C. After drying the granules were free-flowing. Any tendency to agglomerate, particularly with the small granules, indicated that all of the oil had not been removed. If necessary, the washing process was repeated to remove the residual silicone oil. The cleaning process was later simplified to washing the granules in mineral spirits and drying in air at 40°C. A final heat treatment in argon at 240°C for sixty minutes removed any remaining water and organic solvents.

**4.3.9 Sizing:** For some applications granule sizing may not be required, however, fine and/or coarse granules could easily be removed by sieving if required. Furthermore, it was demonstrated that rejects (any non-spherical granules, pieces, or agglomerates) could be sorted by tilting the sieve and allowing the spherical granules to roll across the sieve. The rejects tended to remain on the screen rather than roll across the screen. Several repetitions of this sorting process were very effective at sorting out most of the rejects.

## 4.4 Hydrogen Cycling Tests

**4.4.1 Test Procedure:** The granules were heated to 240°C for sixty minutes prior to the cyclic testing. This removed any water or organic residue from the granules. The granules were cycled in hydrogen five times to evaluate their hydrogen absorption capacity, hydrogen exchange rate, and dimensional stability. The test procedure will be described in a report to be issued by L. K. Heung.

**4.4.2 Hydrogen Test Results** The tests indicated that the external gelation process did not affect the hydrogen storage capacity of the metal hydride particles. The test results will be described in a report to be issued by L. K. Heung.

## 4.5 Granule Characterization

Granules were characterized before and after hydrogen cycling tests with an optical stereomicroscope. Selected samples were examined with a scanning electron microscope (SEM). In order to observe the granules with the SEM, the granules were mounted on two-sided tape and carbon coated. Some of the granules were intentionally fractured to observe internal cross-sections.

The metal hydride particles were in intimate contact with the silica matrix in the granules. These granules exhibited good hydrogen absorption and desorption behavior but some of the granules began to break-up after only five cycles. Microstructural examination with the SEM indicated that although many of the granules remained intact, most were badly microcracked as shown in Figure 16. The porous, brittle silica matrix did not have enough strength to withstand the stress resulting from the expansion that occurred when the metal alloy absorbed hydrogen.

## 4.6 Product Improvements

Hydrogen cycle tests indicated that some of the granules were beginning to break-up after only five cycles. The unbroken granules were microcracked and fragile. Therefore, an important goal of this program was to modify the composition or structure of the sol-gel / metal hydride composite to produce granules that were dimensionally stable and remained integral after hydrogen cycling.

**4.6.1 Requirements** The key to improving the dimensional stability of the granules was selecting materials and processing conditions that would not degrade the ability of the metal alloy particles to absorb hydrogen. Hence, additives had to be chemically compatible with the metal hydride as well as having the required physical properties. Any coatings would have to be porous enough to allow for the rapid permeation of hydrogen. Processing changes had to be adaptable to scale-up for production but could not involve process changes such as high temperature treatments that would oxidize the metal hydride alloy or otherwise alter its composition.

**4.6.2 Methods Considered But Not Tested:** Several methods to improve the dimensional stability of the granules were considered but were not tested experimentally.

**4.6.2.1 Ductile Matrix:** One method was modifying the composition of the matrix in order to add some ductility. This appeared feasible based on studies that indicated that polydimethylsiloxane could be added during the fabrication process to produce sol-gel materials with some ductility.<sup>10, 11</sup> It was considered unlikely that the matrix would have enough ductility to accommodate the large expansion of the metal hydride particles.

**4.6.2.2 Ductile Coatings:** The possibility of coating the metal hydride particles with a porous, ductile material was also considered. This was not pursued since porous coatings produced by processes such as electrochemical deposition have little ductility.

**4.6.2.3 Brittle Coatings:** Another option was coating the metal hydride particles with a very porous, fragile material that would break-up without transmitting enough stress to the matrix to fracture the granules. It would be difficult to develop a coating that was strong enough to remain intact during processing but fragile enough to break-up when stressed in the composite granules.

**4.6.2.4 Porous Shell:** Encasing the granules in a porous but mechanically strong shell was also considered a viable alternative. This approach is being pursued in another study.<sup>13</sup> Glass micro-spheres encasing metal hydride particles will be produced.

**4.6.3 Methods Evaluated Experimentally:** The following methods were evaluated experimentally to improve the ability of the granules to withstand the volume changes of the metal hydride.

**4.6.3.1 Heat Treatment:** Granules were heat treated to strengthen the matrix. The granules were heated to 400°C in an argon atmosphere. This heat treatment reduced the absorption capacity of the metal hydrides to approximately one third of their original capacity, probably due to the closure of porosity as the matrix was densified. Moreover, the heat treatment was not effective in eliminating microcracking (Figure 17) despite the reduction in hydrogen absorption. This effort was abandoned since it was apparent that lower temperatures would not be effective and, although higher temperatures could strengthen the matrix, the ability of the composite to absorb hydrogen would be further compromised.

**4.6.3.2 Pore Formers:** The second process modification utilized a removable pore former to create a gap between the metal hydride particles and the silica matrix. The gap created around the metal hydride particle would allow them to expand without stressing the matrix. Coating the metal hydride particles with a material that could be removed in-situ after fabricating the granules appeared to a reasonable approach based on earlier work.<sup>3</sup>

The first tests to introduce a pore former were performed using 1-dodecanol. Since this material has a melting point of 25°C, it could easily be converted from a liquid to solid. It has a boiling point of only 255°C so it could easily be removed by evaporation to leave a gap around the metal hydride particles. A warm (30°C) suspension of 1-dodecanol liquid and metal hydride particles was sprayed to form an aerosol. When the aerosol was sprayed into cool (20°C) colloidal silica / water, the small 1-dodecanol droplets solidified rapidly as they were cooled. This produced a mixture that contained solid dodecanol/metal hydride granules dispersed in the colloidal silica in water. Drops of this mixture were injected into a column containing hot, high viscosity silicone oil. This approach was not successful because the colloidal silica did not gel rapidly enough to prevent the dodecanol/LANA and silica/water suspensions from segregating. Since dodecanol and water are immiscible and have different densities, as soon as the

dodecanol melted, the small droplets of dodecanol/LANA suspension coalesced, rose to the top of the drop, separated from the water/silica suspension, and dispersed into the silicone oil.

The approach of creating a gap around the metal hydride particles was not abandoned, but rather redirected on using organic materials that would not melt during the external gelation process. Methods were evaluated to produce very small agglomerates of metal hydride particles in an organic matrix. The method selected required that an organic material be dissolved in alcohol and mixed with the metal hydride particles. The cake formed by drying the mixture could be forced through a sieve to produce small agglomerates.

A pore former material with the following properties was required for this granulation procedure:

- a melting point greater than the silicone oil temperature in the column,
- a relatively low boiling point (<350°C) so that the material could be removed without sintering the silica matrix and closing the porosity,
- a relatively simple organic compound whose decomposition products would not poison the metal hydride,
- soluble in alcohol so that it could be dissolved and coated on the metal hydride particles, and
- insoluble in water so that it would not dissolve in the aqueous feed slurry.

Four organic materials were evaluated based on a review of data tables that summarized the physical properties of organic materials. Micronized paraffin wax, DL-camphor, D-camphor, and abietic acid were tested. Small quantities of granules were produced by dissolving these materials in ethanol, mixing the LANA particles into the liquid, drying at 40°C, and then forcing the dried mixtures through a 325 mesh sieve.

The burnout characteristics of the organic materials were determined using thermogravimetric analysis (TGA). The TGA measured the weight loss as a function of temperature as the materials were heated in argon. Based on these tests, abietic acid was selected as the best organic additive because of its relatively low burn-out temperature. The TGA scan shown in Figure 18 indicates that most of the abietic acid was removed between 200°C and 300°C in argon at 10°C/min. It was considered desirable to evaporate the organic slowly to minimize the possibility of a pressure build-up in the fragile granules. The TGA scan in Figure 19 indicates that all of the abietic acid could be removed by heating to 240°C in argon and holding for 60 minutes. This heat treatment schedule also slowed the evaporation rate by a factor of three. The relatively low temperature heat treatment in argon also eliminated the possibility of oxidizing the metal hydride or closing the porosity. Burn-out tests with granules containing abietic acid indicated that granulation did not affect the evaporation rate of abietic acid.

The amount of abietic acid required as a pore former was first calculated based on the known volume expansion of the metal hydride, the worst case metal hydride particle size,

and an assumption of the total surface area of the metal hydride particles. It was calculated that an abietic acid to LANA weight ratio of at least 1:20 was required if the abietic was perfectly distributed as a coating on the metal hydride particles. It was realized that a higher pore former concentration would be required for the actual process.

Tests were performed at incremental pore former concentrations. In the initial tests of this concept, an abietic acid to LANA ratio of 1:10 demonstrated a significant improvement in the integrity of the granules after five cycles in hydrogen. Testing was later performed at ratios of 1:5, 1:4, 1:2, 4:3 in granules with metal hydride concentrations from 20 to 50 wt.%. The optimum abietic acid to LANA ratio for granules containing 40 wt.% LANA was determined to be 1:4. Higher abietic concentrations were not effective in reducing microcracking and the additional porosity weakened the granules.

Although the pore former additions were effective in preventing the granules from breaking up, microcracks were still apparent on the surface of the granules as shown in Figure 20. With no pore former additions or if the pore former had not been effective, the most severe stresses and cracking would be expected to originate in regions of the granules that contain the highest concentration of metal hydride particles. Microstructural analysis of the granules after hydrogen cycle tests (Figure 21) suggested that the cracks did not appear to originate from the larger clusters of metal hydride particles. These agglomerates of metal hydride particles had been held together with the pore former. The cracking could be attributed to individual metal hydride particles that were distributed throughout the matrix and were probably not coated with any pore former. These particles resulted from the rather crude granulation process that was used to produce these small batches of material. Large-scale, commercial granulation processes should be more effective at reducing the concentration of fine, uncoated metal hydride particles.

**4.6.3.3 Sol-gel Coating** Although the addition of the pore former was effective at eliminating the break-up of the granules after exposure to hydrogen, the granules were still weakened by microcracking. The coating technique that was tested with the freeze granulated material formed a relatively thick coating that was often cracked and did not appear to be effective as a means to strengthen granules. It was determined that a very thin polymer sol-gel coating should be applied after the granules had been cycled in hydrogen. It was postulated that the coating would penetrate into the microcracks and strengthen the fragile granules. In addition, the very small porosity in the polymer sol-gel coating offered the potential of acting as a filter for metal hydride poisons while still allowing rapid permeation of hydrogen.

A coating technique was developed to apply a thin layer of a polymer sol-gel on granules that had been cycled in hydrogen. A thin layer of granules was placed onto a 325-mesh sieve over a catch pan. Tetraethoxysilane (TEOS) was poured over the granules three times, shaking the sieve to redistribute the granules between each cycle. The goal was to saturate the granules with TEOS. The TEOS was removed from the catch pan and replaced with water. The sieve with the TEOS saturated granules was placed on the catch

pan containing water and a lid was placed over the granules. The water was heated on a hot plate until condensation was observed on the lid to expose the TEOS coated granules to water vapor. The TEOS reacted with the water to form a polymer sol-gel coating. The closed system was removed from the hot plate and set aside for five minutes after which the sieve containing the granules was removed, dried at room temperature for two hours and at 40°C in air for an additional two hours.

The coating improved the strength of the granules. The strength of the granules was based on relative comparisons of the force required to crush the granules with a small spatula while observing the granules with the stereomicroscope. The granules were cycled in hydrogen five more times and did not appear to lose any strength after cycling. A micrograph of the granules that had been cycled five times before and after coating is shown in Figure 22.

#### **4.7 Hydrogen Absorption Tests**

Testing will be performed to determine if the colloidal silica matrix and polymer sol-gel coating protects the metal hydride particles from poisons such as carbon monoxide. Approximately 40 cc of granules containing 40 wt.% LANA and coated with a polymer sol-gel were produced for these tests. The test procedure and results will be described in a report to be issued by L. K. Heung.

### **5.0 SUMMARY**

The flowsheet that was developed to fabricate sol-gel / metal hydride composite granules is presented in Figure 23. This flowsheet consistently produced dimensionally stable composite granules. The pore former reduced the stresses to the matrix and eliminated the break-up of the granules during hydrogen cycling tests. The polymer sol-gel coating improved the strength of the cycled granules.

A schematic of the external gelation apparatus including the column, feed system, and oil-recirculating system is shown in Figure 24. This schematic includes the optimum design and dimensions for this process.

A wide range of process parameters and column designs were evaluated in the external gelation tests. Many of the critical process parameters and column design specifications were interdependent. The optimum process conditions are summarized in Table 2. Although this set of parameters is referred to as the “optimum” conditions, a similar set of process parameters could be established if, for example, it was necessary to reduce the column height for installation in an existing facility. The oil viscosity could be increased

to decrease the settling rate or the oil temperature could be increased to increase the gelation and drying rates.

The external gelation process could be used for applications that require granules with a porous matrix containing any type of particulate materials. Applications in which the particulate material absorbs either a gas or soluble ions from solution should be considered. The matrix material must be available as colloidal particles. Fairly large particulates, up to 100 microns, could be dispersed in these granules.

## 6.0 FUTURE WORK

The hydrogen testing of the granules still needs to be completed. The test procedures and results will be documented in a report to be issued by L. K. Heung.

Additional experimental work is needed to optimize the coating technique. Most of the experimental work to optimize the external gelation process has been completed but additional testing is needed to establish the process limits.

The capability to mill metal hydrides under a controlled atmosphere is currently being established by MTS. This will significantly decrease the time and cost to produce fine metal hydride particles.

The next step in process scale-up should focus on using commercial process equipment to granulate the abietic acid with the metal hydride particles. One of the key criteria in selecting the granulation process should be the minimization of fines.

In order to increase the production rate in the column, multiple feed locations will be required. A low flow, digital, multi-channel peristaltic pump is required to accurately control the slurry feed rate to multiple feed tubes. The incoming oil must be split into multiple streams so that the each slurry feed tube can be injected into an oil stream. The diameter of the column must be increased to accommodate a bundle of 1" to 2" diameter glass tubes that are long enough to isolate the feed streams until the granules are firmly gelled.

The temperature control of the column could be improved by using digitally controlled thermostats. The size of the opening in the bottom of the column should be increased from  $\frac{1}{4}$ " to  $\sim\frac{1}{2}$ " to accommodate the increased production rate of granules. The larger opening would also be needed to increase the oil discharge rate to supply the multiple oil streams. Similarly, the dimensions of the coil would have to be modified to balance the oil discharge and return rates.



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Dr. George Wicks provided guidance in the processing of sol-gels.

Jack Durden performed the sample preparation and operated the scanning electron microscope.

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**Figure 1: Freeze granulated SiO<sub>2</sub> / LANA**



**Figure 2: Surface of freeze granulated  $\text{SiO}_2$  / LANA**

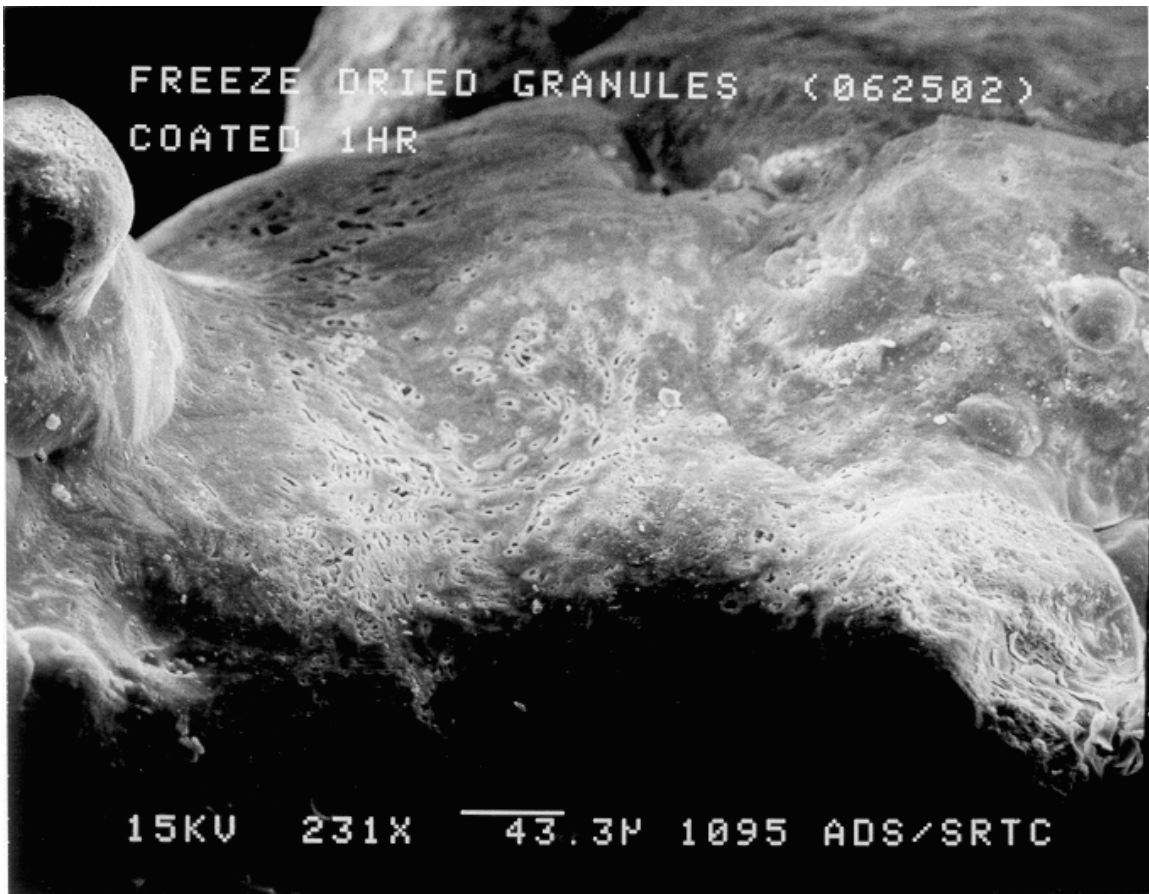
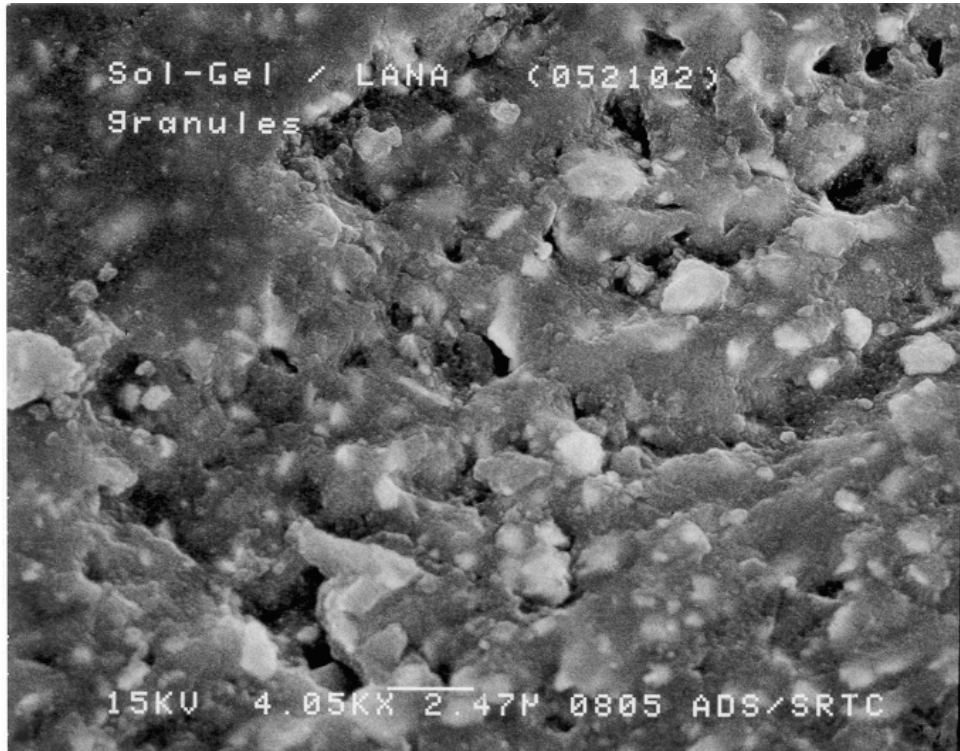


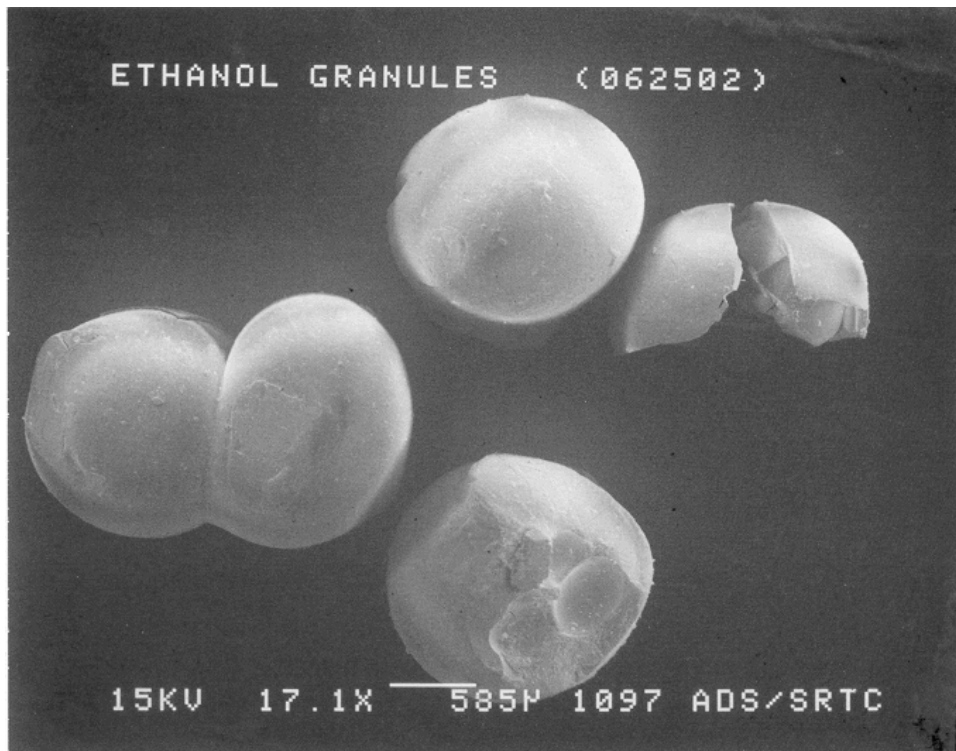
Figure 3: Freeze Granulated  $\text{SiO}_2$  / LANA with 1-hour dip coat in polymer sol-gel



**Figure 4: SiO<sub>2</sub> / LANA granules produced by external gelation. Note “blow-out” type flaws resulting from excessive drying rate. (Optical micrograph @ 10X)**



**Figure 5: Microstructure of a SiO<sub>2</sub> / LANA granule produced by external gelation**



**Figure 6: SiO<sub>2</sub> / LANA granules produced by external gelation from ethanol-based slurry**

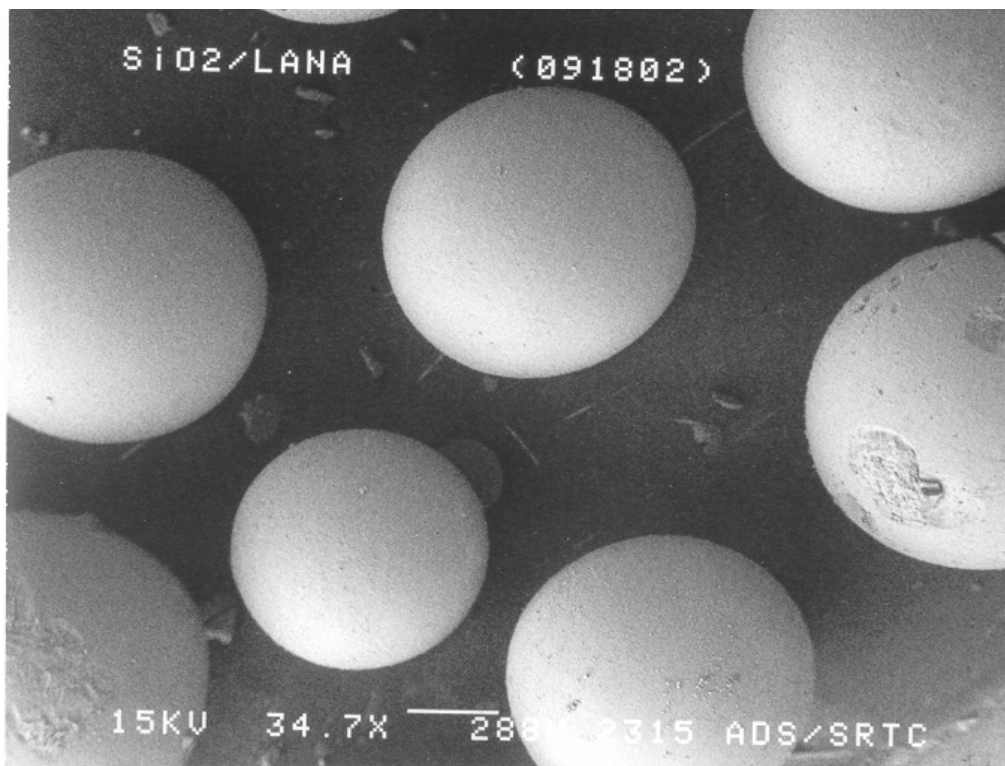




**Figure 7: Peristaltic pump feed system**



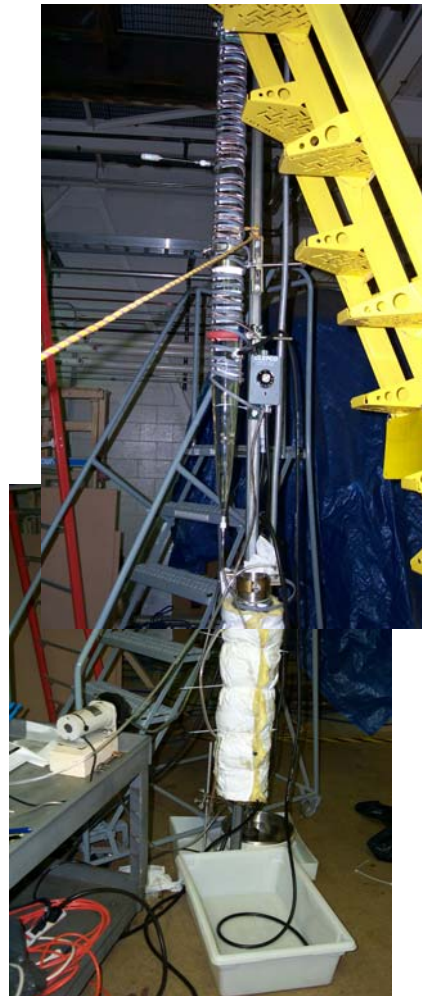
**Figure 8: Low pressure air feed system**



**Figure 9: SiO<sub>2</sub> / LANA granules with a narrow size distribution produced by external gelation**



Top Section



Base Section

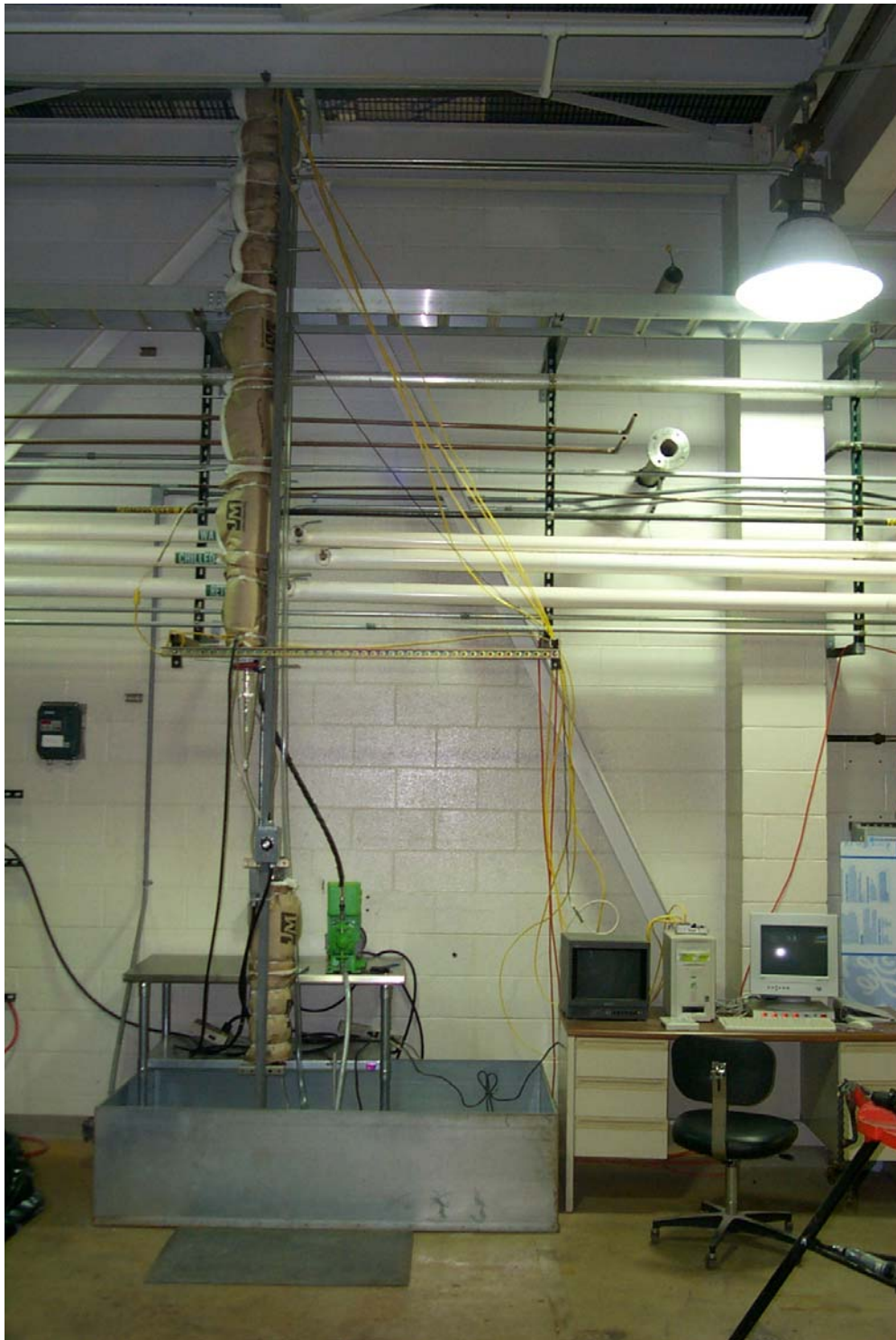
**Figure 10: 18' tall glass column at CETL (composite photographs). Top section includes feed system and insulated portion of column. Base section includes insulated coil but the bottom of the column was still under construction and was not yet insulated.**



**Figure 11: Top section of 27' column at the third level of the CETL high bay.**



**Figure 12: Mid-section of 27' glass column includes thermostat for upper half of column**



**Figure 13: Base section of 27' glass column includes coil, oil pump, catch pan, video monitor, and computer for data acquisition.**

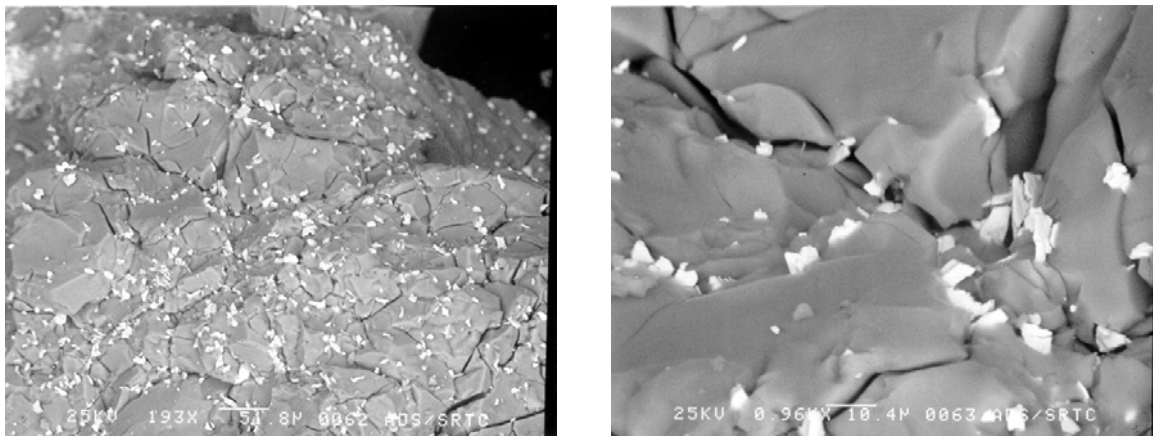


**Figure 14: Granule collection with sieves in oil bath at base of column**

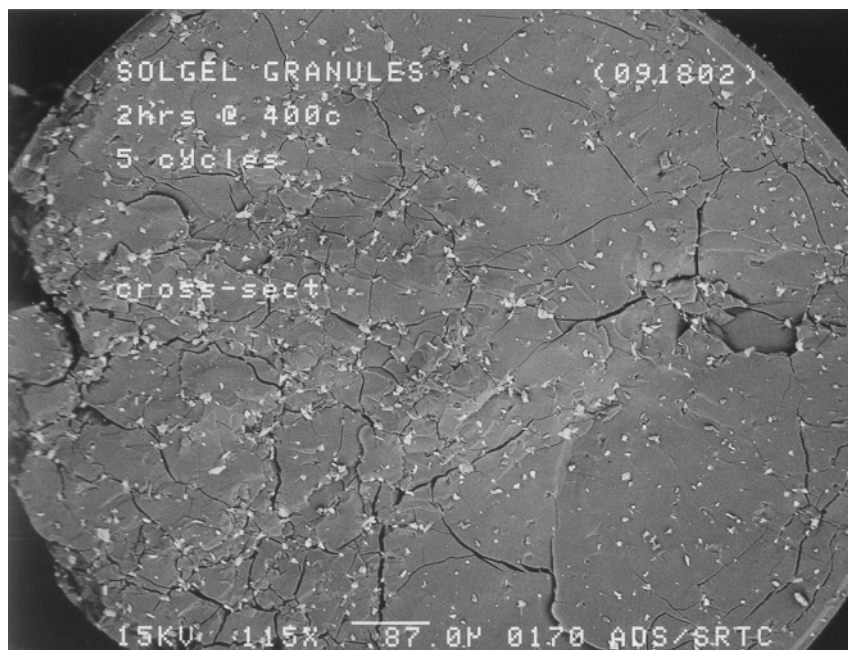




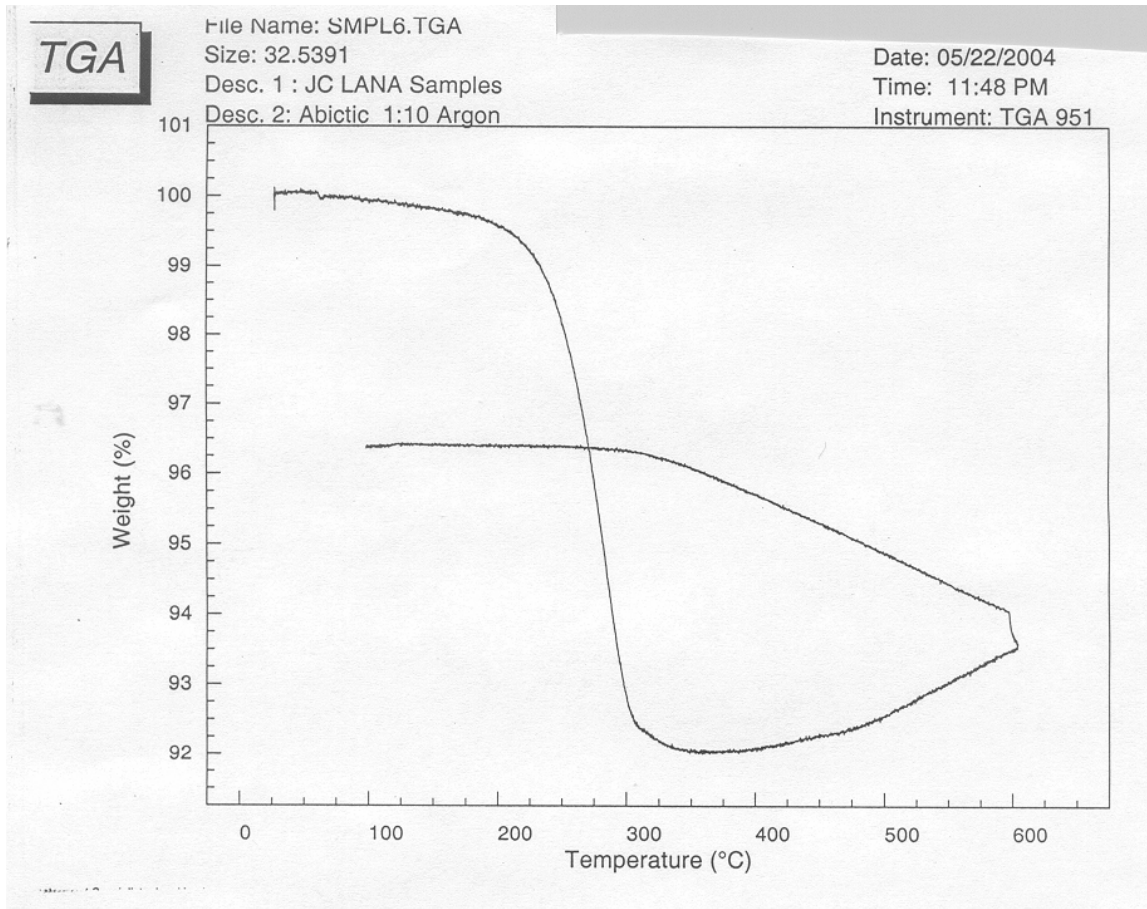
**Figure 15: Heated vessel for blending silicon oil.**



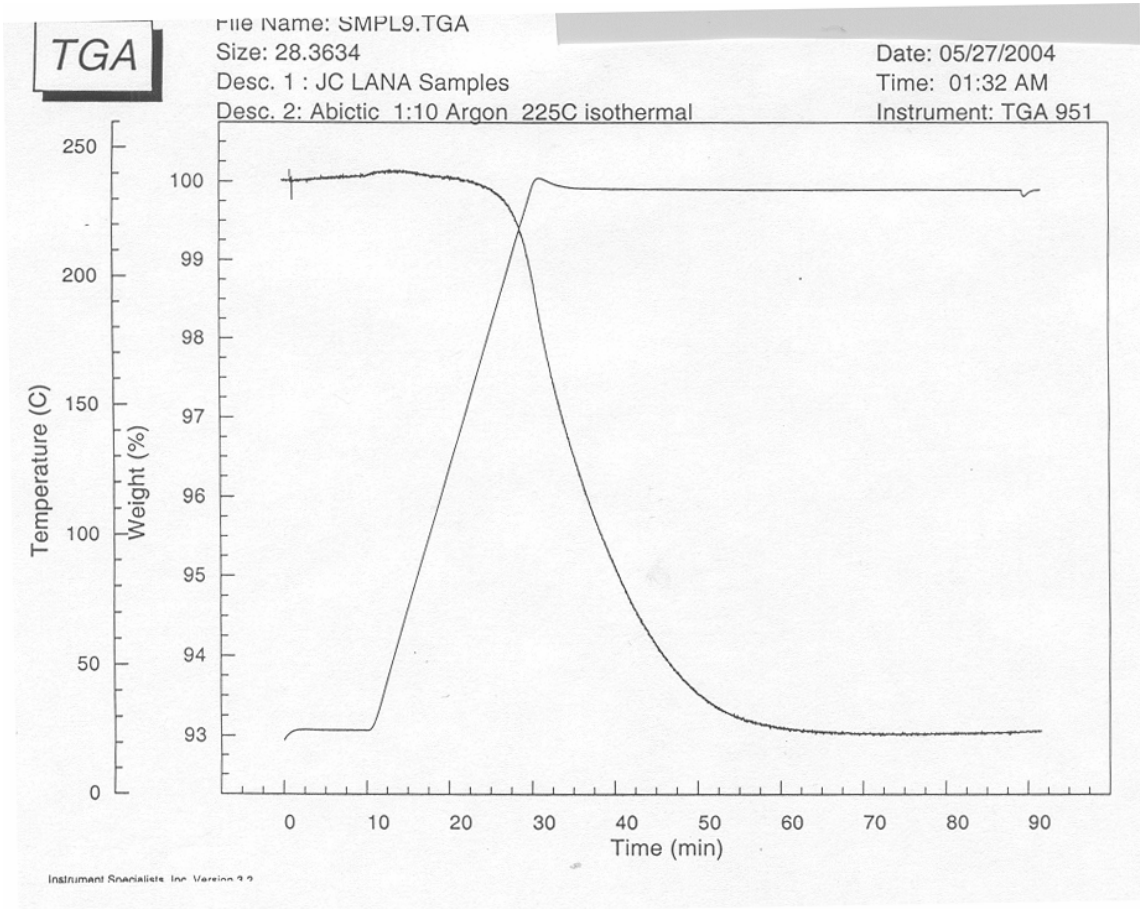
**Figure 16: Microcracking caused by the expansion of LANA particles after five-cycle hydrogen test. LANA appears as white particles in SEM micrographs.**



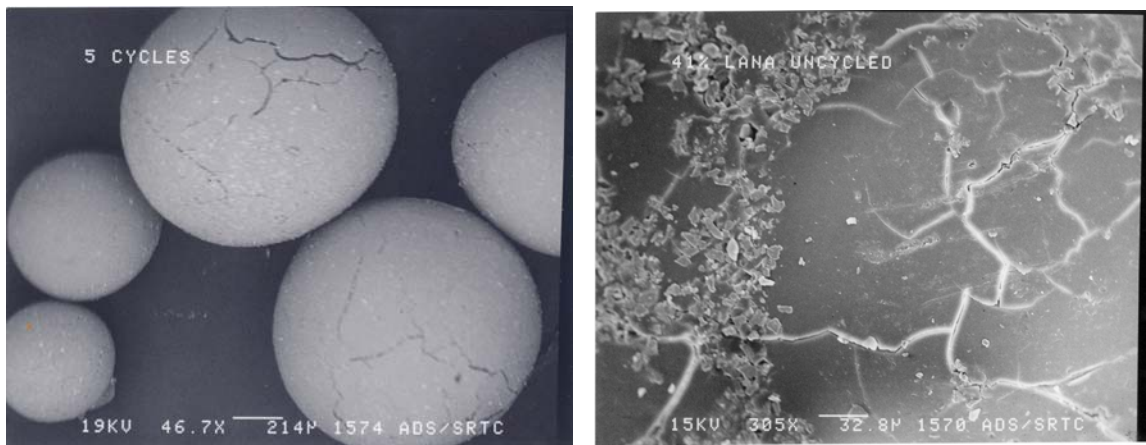
**Figure 17: Microcracks in the cross-section of a granule that was heat treated at 400°C and cycled 5X in H<sub>2</sub>**



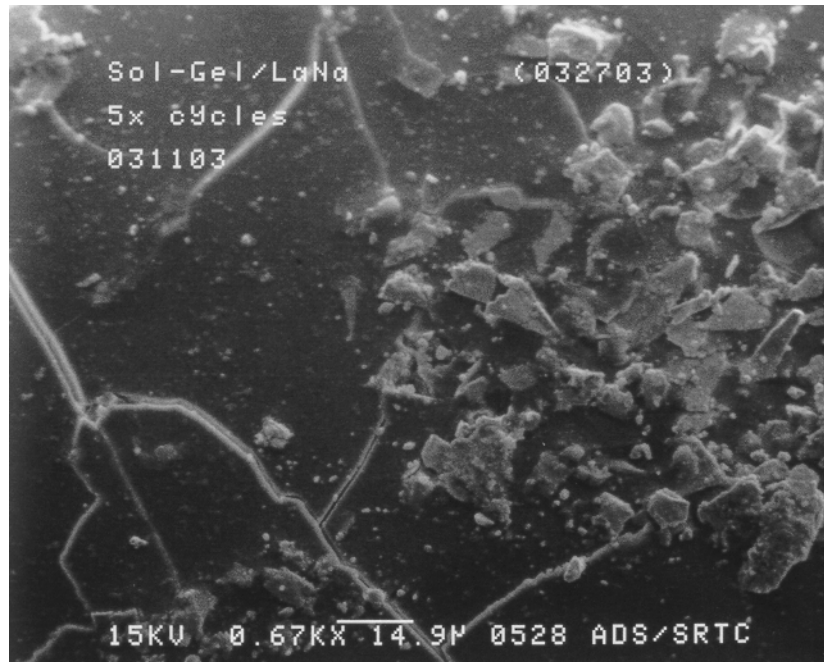
**Figure 18: TGA scan indicates that most of the abietic acid decomposition occurs between 200°C and 300°C when heated in argon.**



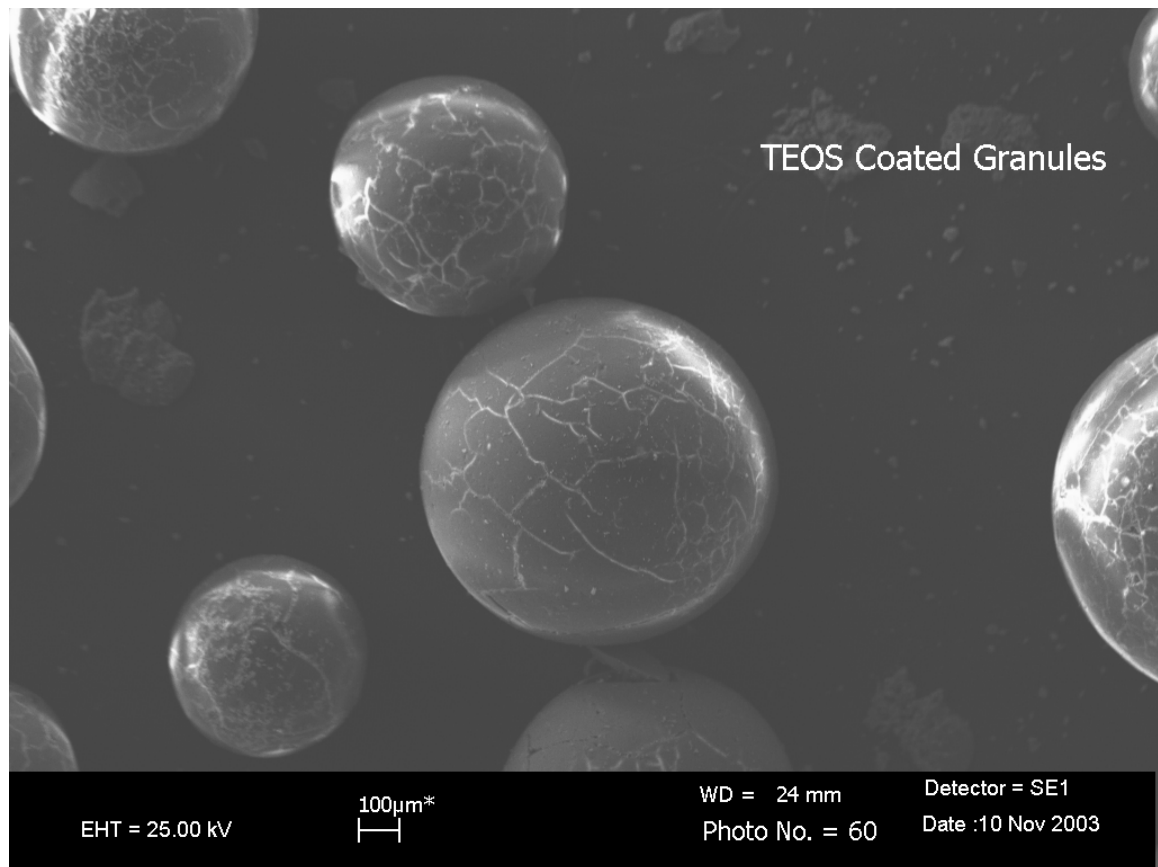
**Figure 19: TGA scan indicates that abietic acid can be removed by heating to 240°C for one hour in argon.**



**Figure 20: Granules fabricated with removable pore former. Five cycles in hydrogen caused microcracking on the surface but the granules remained intact.**



**Figure 21: Large cluster of metal hydride particles does not appear to be the source of microcracks in a granule fabricated with the removable pore former.**



**Figure 22: Granules cycled 5X in H<sub>2</sub>, coated with TEOS, and cycled 5X in H<sub>2</sub>. Although the thin, transparent coating could not be resolved at high magnification with the SEM, the coated granules appeared darker and shinier.**



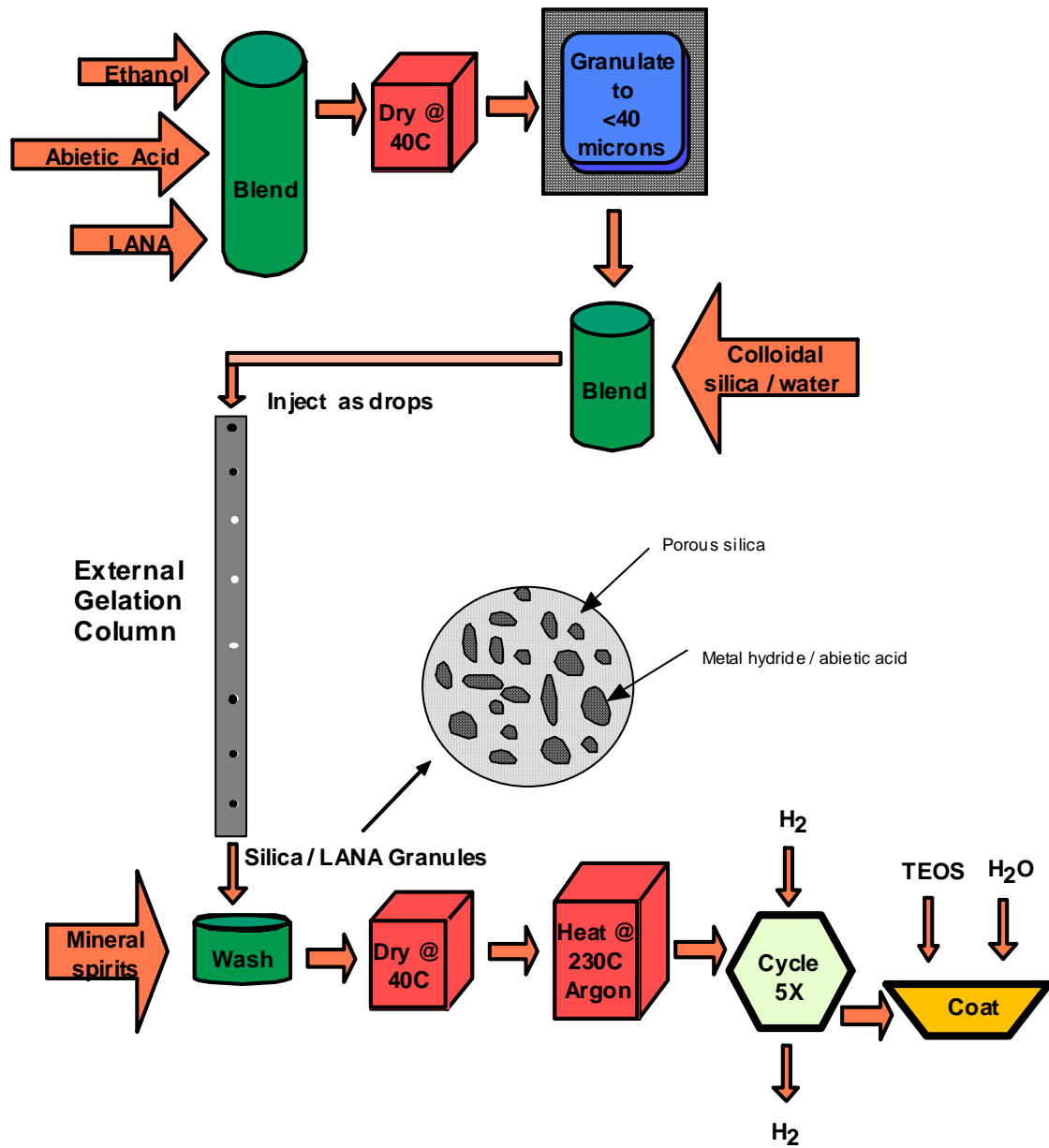


Figure 23: Process flowsheet to fabricate sol-gel / metal hydride granules

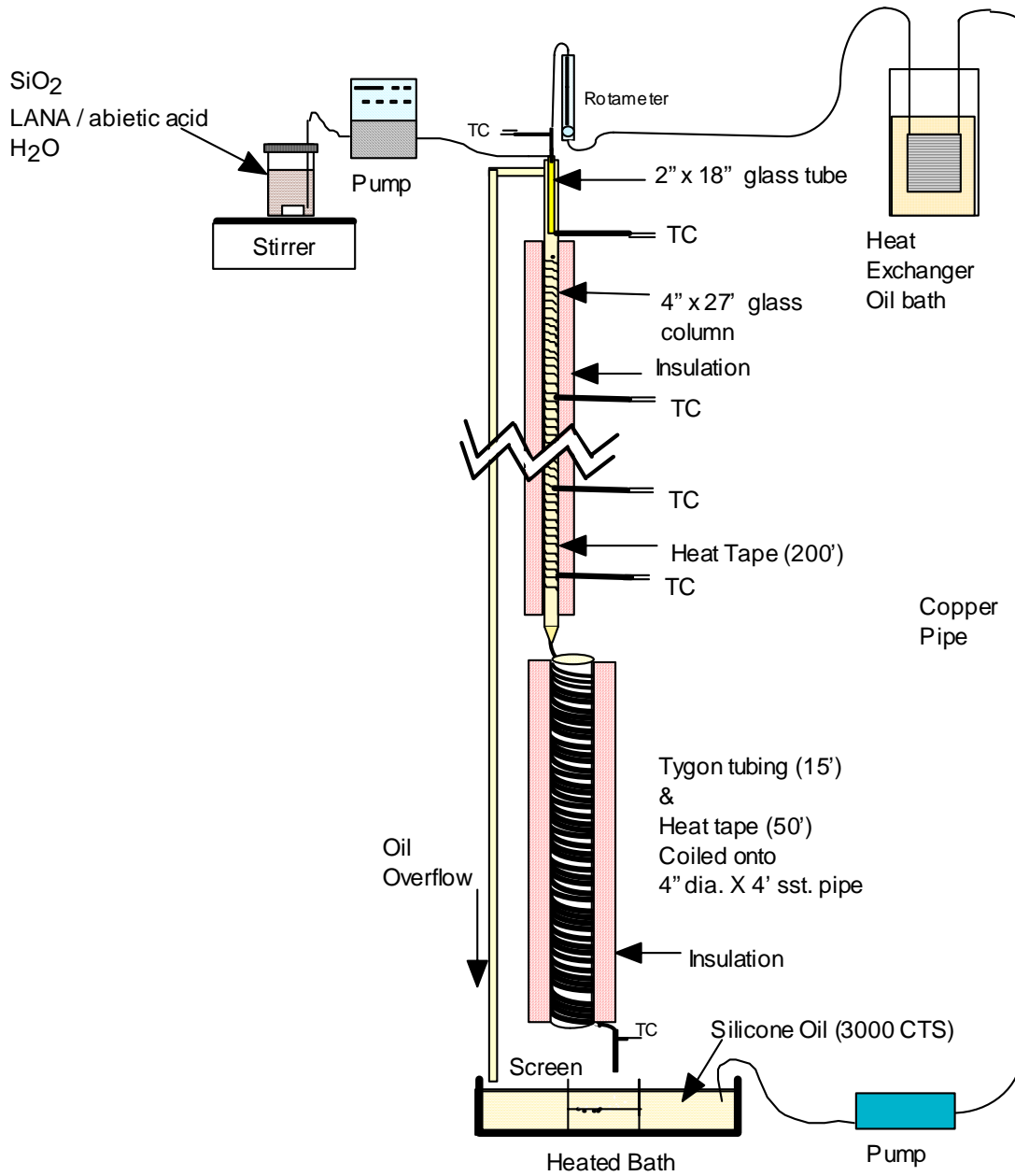


Figure 24 : Schematic diagram of external gelation column

**Table 1: External gelation test parameters**

| <u>Process Variable</u>  | <u>Test Conditions</u>   |
|--------------------------|--|
| Column height            | 8', 16', 18', 27'  |
| Column diameter          | 2", 4"   |
| Column materials         | PVC, steel, glass  |
| Coil length              | 15', 30', 100'   |
| Feed system              | Pipette,<br>Micro-peristaltic pump,<br>PTFE peristaltic pump,<br>Low pressure regulator  |
| Feed injection           | Feed directly into oil in the column<br>Side feed into incoming oil feed tube<br>Concentric feed within oil feed tube<br>Side feed below oil feed tube |
| OD of oil feed tube      | 1/4", 3/8"   |
| Oil viscosity            | 50 to 5000 CTS   |
| Incoming oil temperature | 40°C to 92°C   |
| Column oil temperature   | 69°C to 97°C   |
| LANA content             | 20 to 50 wt.%  |
| Granule washing          | Hexane followed by ethanol<br>Mineral spirits  |

**Table 2: Optimum process parameters for sol-gel / metal hydride granule fabrication by external gelation**

| <u>Process Variable</u>     | <u>Optimum Condition</u>  |
|-----------------------------|---|
| Column height               | 27'   |
| Column diameter             | 4"  |
| Column materials            | glass   |
| Coil dimensions             | 15' long, 4" dia. coil, 3/8" dia tubing                                       |
| Feed system                 | Micro-peristaltic pump  |
| Feed injection              | Side feed into incoming oil feed tube   |
| OD of oil feed tube         | 1/4"  |
| Oil viscosity               | 3000 CTS  |
| Incoming oil temperature    | 40°C  |
| Column oil temperature      | 70°C  |
| LANA content                | 40 wt.%   |
| LANA/Abietic acid wt. ratio | 4:1   |
| Granule washing             | Mineral spirits   |
| Granule heat treatment      | 240°C, 1 hour in argon  |
| Coating                     | H <sub>2</sub> cycle 5X, saturate with TEOS, absorb H <sub>2</sub> O, air dry |