

Formation of Inorganic Precipitates in Microgravity on the STS-40

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A payload for the space shuttle was designed to investigate the effects of microgravity upon formation of inorganic chemical precipitates; it was constructed, tested, flown, and analyzed. The payload met all NASA safety requirements and passed preflight testing. After extensive delays, the payload was flown aboard orbiter Columbia on STS-40. The launch was 1991 June 5, and the flight duration was 9 days. The payload and data (film and chemical reaction chambers) were retrieved on 1991 July 15-16, and returned to the Frontiers of Science Foundation in Oklahoma City. Precipitates analogous to those prepared on board the Columbia were prepared on earth for comparison. The surface of each precipitate was examined by scanning electron microscopy. The major difference in the precipitates prepared in microgravity versus those prepared on earth is that the former generally exhibit much larger or more well-developed particles. Photographs of the images of the samples are presented for comparison.

INTRODUCTION

In late 1983, the Frontiers of Science Foundation in Oklahoma City sponsored a statewide competition among high school students to conceptualize a payload for space research - an experiment to fly as a Getaway Special. A group of faculty members in various disciplines at Oklahoma State University selected "Precipitates in Zero Gravity" as a project best utilizing the space environment. Two juniors at Casady School in Oklahoma City had proposed the investigation of the formation of inorganic chemical precipitates in the microgravity environment. The Foundation funded the payload development at Oklahoma State University and, after a two-year developmental period, the payload was ready for flight.

The ever-increasing use of the microgravity environment in materials research prompted the investigation of the formation of inorganic precipitates. The payload designated G-405 utilized six transparent chemical reaction chambers in order to mix a dry powder with a liquid solution. At intervals the progress of the precipitate formation was photographed. The purpose of this experiment was to photographically record the formation of several types of chemical precipitates in the microgravity environment.

The reason for experimenting with precipitates in microgravity was to collect data which could be studied and used to predict the outcome of other similar reactions in space. In addition, this experiment allowed basic research into chemical reactions which are affected by gravity on Earth. The various tasks performed during the 14-hour duration of the experiment were initiated and monitored by a custom-built digital controller. The payload was flown aboard orbiter Space Transportation System (STS)-40 with a launch data of June 5, 1991, and a duration of 9 days. The precipitate particles were analyzed post-flight by using scanning electron microscopy (SEM) at the University of Oklahoma.

METHODS

Payload G-405 was originally scheduled as first backup payload for STS-61C for a March, 1986, flight. (This was the flight immediately following the last flight of the Challenger.) To meet this schedule, the completed payload was shipped to Kennedy Space Center in November, 1985. The payload was stored at Kennedy Space Center until early May, 1988, when it was temporarily sent to Louisiana Tech University. The payload withstood the 2.5-year dormancy. The payload was originally shipped

without the chemicals so the chambers and seals were still in new condition. The battery pack was the only component which showed any signs of age. The cells used were the Gates "X" cells, each with 2 V and 5 A h capacity. The cells were combined to provide a nominal 12 V and 20 A h capacity. When shipped, the batteries were charged to approximately 13 V. After 2.5 years in storage, the batteries had discharged to about 11 V but the current capacity was greatly diminished. The battery pack was capable of driving the camera autowinder only several times before failing. After voltage tests were performed on individual cells, four of the cells were found to be discharged severely (output less than 1 V) and were not rechargeable. These four cells were replaced. All other lower voltage systems such as the flash and the digital controller were still functional. This exhibited the excellent shelf life of the lead-acid battery. In February, 1991, the payload was returned to Cape Canaveral, and it was flown aboard orbiter Columbia in June, 1991.

The precipitation reactions which were carried out in the payload are shown below. The first compound is the dry powder for that chamber, the second compound is the solute (in water), and the fourth compound is the precipitate formed in that chamber. The following six chemical reactions used were:

- 1) $\text{MnSO}_4 + 2\text{KOH} \rightarrow \text{K}_2\text{SO}_4 + \text{Mn}(\text{OH})_2 \downarrow$
- 2) $\text{NiCl}_2 + 2\text{NaOH} \rightarrow 2\text{NaCl} + \text{Ni}(\text{OH})_2 \downarrow$
- 3) $\text{MnSO}_4 + \text{Ba}(\text{OH})_2 \rightarrow \text{Mn}(\text{OH})_2 + \text{BaSO}_4 \downarrow$
- 4) $\text{K}_2\text{Cr}_2\text{O}_7 + 2\text{AgNO}_3 \rightarrow 2\text{KNO}_3 + \text{Ag}_2\text{Cr}_2\text{O}_7 \downarrow$
- 5) $\text{Hg}(\text{NO}_3)_2 + 2\text{NaCl} \rightarrow 2\text{NaNO}_3 + \text{HgCl}_2 \downarrow$
- 6) $\text{NaCl} + \text{AgNO}_3 \rightarrow \text{NaNO}_3 + \text{AgCl} \downarrow$

Precipitate formation first depends on the presence of a solution which is saturated with a relatively insoluble salt. If the solution is supersaturated, the salt will precipitate until the solution is once again saturated. In the gravity environment this process is very dependent upon localized concentrations within the supersaturated solution. As heavier particles of precipitate settle out, the solution may be physically mixed, which aids in precipitate formation, or the solution may become stratified, which will create zones of precipitation similar to the nucleation sites within a solidifying metal alloy. In the microgravity environment though, the precipitate formation is dependent only upon the localized solution concentration. This, of course, assumes constant temperature throughout the solution. The data from the precipitate formation were taken by means of photographs of the formation as well as post-flight analysis of the precipitate particles.

The precipitates were classified under the forms of gelatinous, crystalline, or curdy (2). Gelatinous precipitates are formed because of the cation's high hydration energy in the precipitate. In the crystalline precipitate, the smaller particles are more soluble than the larger ones and therefore have fewer growth sites allowing more uniform formation. Curdy precipitates form because the initial (small) precipitation particles have nearly the same solubility as the larger particles. This allows many centers of formation leading to a flocculated colloid. The formation of all three types of precipitates is affected by gravity, which can inhibit or overshadow other growth mechanisms.

RESULTS and DISCUSSION

Precipitates analogous to those made on board the Columbia were prepared in the laboratory under the same conditions (except gravitational). The chamber containing reaction 2 was deactivated prior to flight due to a minor leak, precluding investigation of reaction 2. According to the SEM elemental x-ray analyses, the precipitates formed in chambers 4 and 6 showed significant contamination with iron (chambers 4 and 6) and silicon (chamber 6); these reactions were not studied. This left three reactions for study: 1, 3, and 5, described above.

Manganese Dihydroxide (Chamber 1): Manganese dihydroxide $\text{Mn}(\text{OH})_2$ is a gelatinous precipitate, which is formed because of the cation's high hydration energy in the precipitate (2,3). X-ray elemental analyses of the manganese dihydroxide precipitates formed aboard the Columbia and in our laboratory showed the expected prominent signals for manganese. This sample also showed a very small silicon peak, possibly due to contact with a material used in constructing or coating the chamber which contained the sample.

Pictures of precipitate formed at zerogravity aboard the Columbia and of those formed in our laboratory are compared in

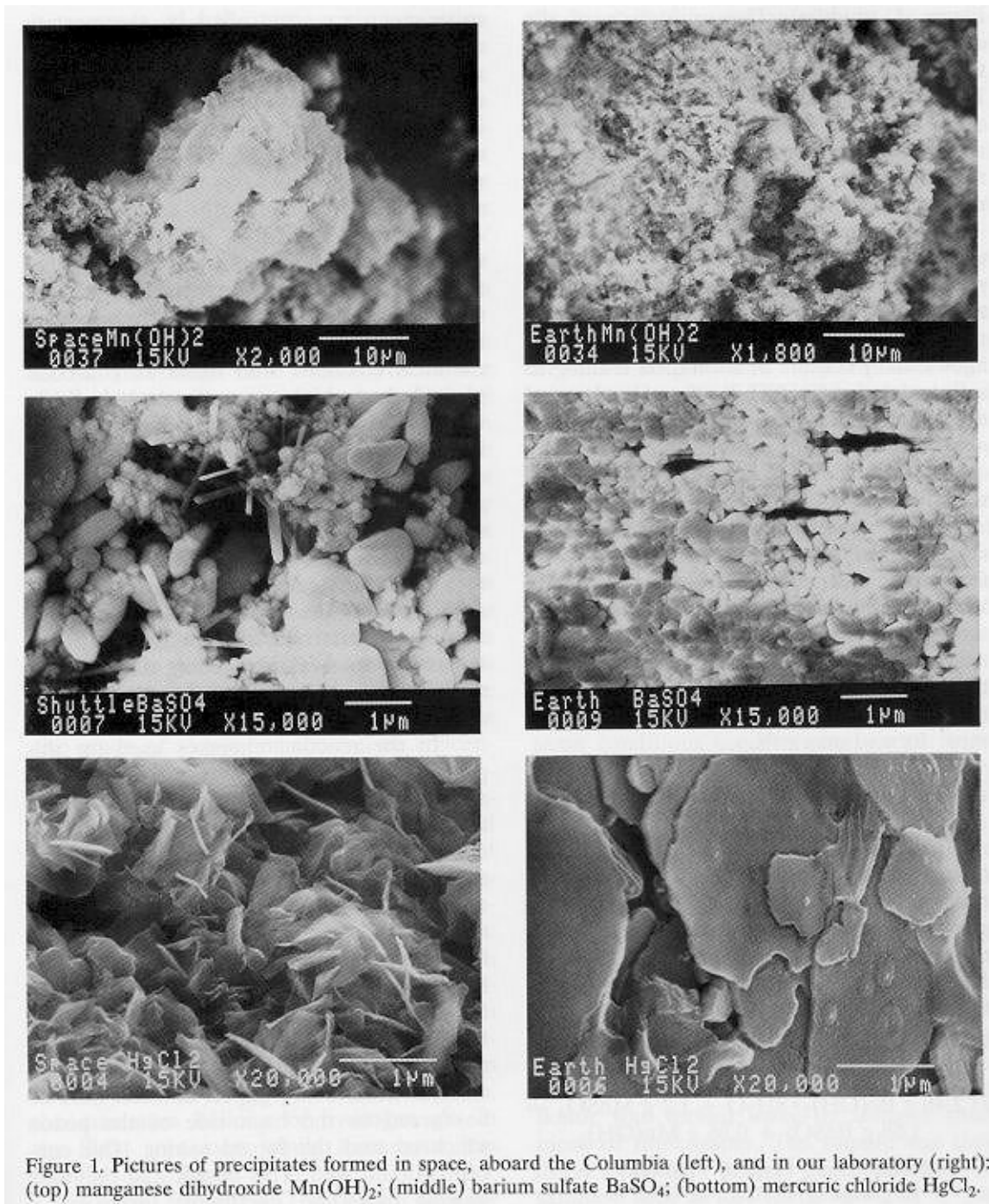


Figure 1. Pictures of precipitates formed in space, aboard the Columbia (left), and in our laboratory (right): (top) manganese dihydroxide $Mn(OH)_2$; (middle) barium sulfate $BaSO_4$; (bottom) mercuric chloride $HgCl_2$.

Figure 1 (top). The earth sample at magnification 1800 \times shows two distinct structures: one is clustered and granular, the other is triangular. The shuttle sample shows only the granular structure, with smaller particle size.

Barium Sulfate (Chamber 3) Barium sulfate $BaSO_4$ is a precipitate in which the smaller particles are more soluble than the larger ones. X-ray elemental analyses of the barium sulfate precipitates formed aboard the Columbia and in our laboratory show the expected prominent signals for barium. However, a marked increase in manganese content is indicated when the beam is focussed on rod-like structures which are obvious in the pictures of the space sample (see below).

Pictures of the shuttle precipitate and of those formed on earth are shown in

Figure 1 (middle). The uniformity of the crystals is apparent in the pictures, and those in the space sample appear larger. The rod-like structures, shown in the picture of the space sample, have a concentration of manganese higher than that of the surrounding mass of precipitate; these "rods" do not appear in the earth sample.

Mercuric Chloride (Chamber 5): Mercuric chloride HgCl_2 is classified as a curdy precipitate. Curdy precipitates form because the initial (small) particles have nearly the same solubility as the larger particles. This allows many centers of formation leading to a flocculated colloid (2,3). X-ray analyses of the mercuric chloride precipitates formed aboard the Columbia and in our laboratory show the expected prominent signal for mercury.

Pictures of the precipitate formed under zero-gravity conditions aboard the Columbia and of those formed in our laboratory are compared in Figure 1 (bottom). The x-ray examination reveals the particles to be loosely aggregated plates in both samples, with those formed in space being larger or more well-developed than those formed on earth.

EXPERIMENTAL PROCEDURES

Chemicals and Reaction Controls: The quantities of chemical reactants and products for the three reactions studied are given below; for each reaction, the first compound was dissolved in 40 ml of water and the last compound remained in solution, in ≈ 40 ml of water.

- 1) $4.5 \text{ g KOH} + 6.1 \text{ g MnSO}_4 \rightarrow 3.6 \text{ g Mn(OH)}_2 + 7 \text{ g K}_2\text{SO}_4$
- 3) $2.46 \text{ g Ba(OH)}_2 \cdot 8\text{H}_2\text{O} + 1.2 \text{ g MnSO}_4 \rightarrow 1.68 \text{ g BaSO}_4 + 0.86 \text{ g Mn(OH)}_2$
- 5) $20 \text{ g Hg(NO}_3)_2 \cdot \text{H}_2\text{O} + 7 \text{ g NaCl} \rightarrow 16 \text{ g HgCl}_2 + 10 \text{ g NaNO}_3$

Each reaction (1, 3-6) took place within a clear Plexiglas chamber. The reactants were separated by a piston and O-ring seal until the chamber was activated by an astronaut. A commercial 35-mm camera, with flash and color film, photographically recorded the precipitate formations over a 13-h period. The reaction chambers and camera were activated by built-in sequencing so that only one operation was required by shuttle personnel. The thermal environment of the experiment was controlled by thermostatically activated resistance heaters. The six reaction chambers were situated throughout a 60-degree segment of one side of the canister. The camera unit was diametrically opposite to the chambers and utilized a 28-mm wide-angle lens so as to photograph all six chambers simultaneously.

Mixing Chambers: The purposes of the six mixing chambers were to allow photographic data of particle formation, to contain the chemical reactants, and to provide a forced mixing of the two reactants in each chemical chamber, and these were accomplished through the use of relatively thick-walled Plexiglas tubing and rubber O-rings. Force-mixing the reactants was a problem of differential volumes within an enclosed cylinder and was approached as a hydraulic system problem. In a conventional hydraulic cylinder, one side of the piston is connected to a rod which exits the cylinder body. The other side of the piston does not typically have a rod attached to it. When the piston is moving, more fluid is being displaced on the non-rod side of the piston than on the side of the piston which contains the rod.

In the reactant chamber used for this payload, it was necessary to use an arrangement which had a rod running the entire length of the cylinder. It was impractical to use a rod of varying diameter to establish the differential volume relationship; this was accomplished by using two sizes of Plexiglas tubing. Upon activation, a cylinder spring forced a piston to move, and the O-ring seal between the chemical reactants was broken. In addition, the downstream chamber half had a slightly larger inside diameter than the upstream chamber half. This open annulus around the piston allowed fluid to be forced to the back side of the piston which created the forced mixing. This concept worked well. This design had only one moving part, and its driving force was a spring which was compressed prior to flight, adding to the system reliability. The cylinder piston contained one O-ring seal to keep the reactants apart prior to activation. The cylinder body also had O-rings in each end to eliminate reactant leakage into the canister interior. The cylinder body also contained absorbent material just outside of the cylinder O-rings to add an additional level of protection against reactant leakage.

To better maintain a constant

temperature within the six reaction chambers, each one was wrapped with two flexible resistance heaters. The heaters were each about two feet long, covered with woven fiberglass, and composed of Teflon-coated wires. Originally designed for use at 120 V AC and 100 W, each heater was operated at 12 V DC and 1 W. The heaters operated at about 32 °C and provided 12 W of power at relatively low temperature. The heaters were thermostatically controlled to become active below 15 °C.

Special Design Considerations: It was necessary to design for a catastrophic failure of all six reactant mixing chambers. Several of the liquid reactants are caustics which readily dissolve aluminum. Because the entire structure of the mixing chambers was made of 6061-T6 aluminum, it was necessary to coat it with an inert resin. To attain flight acceptance, PT-201 from Products Techniques, Inc. was chosen. This resin was brushed on and then baked at 180 °C to expedite outgassing. The coating provided a hard surface which was resistant to caustics and also provided electrical isolation of the structure. Because the flight container was also made of aluminum, the caustic concentration was limited so that there was no possibility of the caustics penetrating the canister thickness. If all of the caustics attacked the canister interior, the wall thickness of the canister would have decreased by one-thousandth of an inch. An additional consideration in the use of the caustics was the release of hydrogen gas upon reacting with aluminum. This consideration was the overriding factor for the maximum concentration of the caustic solutions. The caustic concentration was such that if all of the caustics had reacted with the unprotected aluminum, the maximum buildup of hydrogen gas in the flight containers would have been less than 3% by volume.

Control Circuitry: The control circuitry for the operational scenario of the payload was relatively simple. Upon astronaut activation, the circuitry maintained the reactant chambers in a dormant state for one hour. During this time, the thermal environment of the chambers was stabilized by way of thermostatically controlled chamber heaters. After one hour, the reactant chambers were activated by solenoid and the precipitation process began. During several ground tests, it was learned that it is necessary to record the precipitate formation early in the experiment. Therefore, a photograph was taken once every minute during the first 12 min, then once every 10 min for the next 2 h, then once every 50 min for a total of 36 exposures over a 14-h period. The control circuitry used a simple digital clock, counters, and EPROM memories to control the duration between photographs.

Personnel at Goddard Space Flight Center advised us that some EPROMs are very susceptible to memory damage from radiation. This fact led to the use of three EPROMs to provide a "majority vote" logic scheme. The 2716 EPROM was selected because of its widespread availability and its ease of programming. This 16-k memory chip was programmed with a 40-byte program. Though severely under-utilized, the chip was used because of the availability of the programming hardware. The output of the EPROMs were used as the input to the voting logic. The voting logic was used to address multiplexers so that the appropriate clock pulses activated the camera shutter.

Control Reactions: Precipitates were formed on earth, but otherwise under the same conditions used to generate the samples formed in space. Standard laboratory glassware and apparatus was used to generate the samples on earth.

Electron Microscopy Analysis: The crystals were mounted on JEOL copper bulk electron microscopy sample holders. Double-sided carbon adhesive tape was used to fix the sample crystals to the holder. A drop of the sample containing crystals was placed on the tape, and the crystals were spread thinly and evenly across the area to be scanned. After waiting a few min for the crystals to settle, the excess mother liquor was wicked away by using a small piece of filter paper. The sample was then dried overnight before being scanned. In samples with a low metal content, it was necessary to sputter-coat the sample with Au-Pd to make the sample conductive.

The precipitates were examined, in the Samuel Roberts Noble Electron Microscopy Laboratory at the University of Oklahoma, with a JEOL JSM-880 High Resolution Scanning Electron Microscope equipped with an x-ray detector to facilitate elemental analysis via energy-dispersive x-ray spectroscopy (EDS). Some of the space shuttle samples (chambers 1 and 6) show a very small

silicon peak, possibly due to contact with a material used in constructing or coating the chambers which contained the liquids. Photographs of the images of the samples were obtained for comparison.

Operational Scenario: During loading of the solution into chamber 2, a seal internal to that reaction chamber developed a very minor leak. It was decided to empty that chamber before flight. All other preparations were nominal and the assembly was sealed in the flight can, which was leak checked with 4 psig dry nitrogen. The can was attached to the GAS Bridge the following week, and the bridge was inserted into Columbia on 1991 May 24.

The payload was activated at 18:20 EDT on 1991 June 6 and deactivated at 17:50 EDT on 1991 June 7, a 23.5-h operation. The payload was designed for a 14.5-h operation; however, this extension should have been of no consequence.

As early in the mission as possible and just prior to a 14-h period of minimum gravity, an astronaut activated GCD relay "A" which supplied battery power to all experiment components. The heaters were thermostatically activated to bring the can interior to the proper temperature and continued to be active throughout the experiment. With activation of GCD relay "A", an internal delay timer started counting up to one hour. During this interval the main timing/control clock was inhibited. One hour after relay "A" was activated, the main timing/control clock became active and the spring-loaded mixing chambers were solenoid-activated. During the next 12 min, a picture of the precipitate formation was taken every minute. During the next 2 h, a picture was taken every 10 min. During the next 10 h, 12 more pictures were taken for a total of 36 frames. Total experiment duration was 13 h and 12 min. At 14.5 h after GCD relay "A" was activated, deactivation of the relay by an astronaut removed all battery power and completely shut down the experiment.

Upon retrieval of the payload, we found that all six chambers had activated and that 36 exposures had been taken. However, upon examination of the interior of the flight can, it was obvious that another chamber had leaked. This resulted in some discoloration of the interior of the flight container and slight corrosion or discoloration of exposed, non-protected metallic fasteners. The experiment was not hazardous to any flight operations. Preliminary evidence indicated that the leak took place after the experiment was sealed in the flight can and before it was activated in space. There are several possible reasons for the leak, including excessive operating temperature in orbit. Also, the liquid appeared to migrate toward a vent plug in the flight can, which could indicate the payload was operating under some degree of vacuum. The degree of sealing or leaking of the flight can was determined by NASA at the time of preparation, and the higher than expected operating temperatures were determined by NASA at the time of retrieval.

The leak occurred from chamber 4, which contained 40 ml of 2 molar silver nitrate, and potassium dichromate as powder. The precipitate, silver dichromate, a brown crystalline substance, was responsible for much of the discoloration. From the mass of residue left in chamber 4, it was estimated that a total of 5 to 10 ml of the silver nitrate and/or precipitate escaped from the chamber. The materials appear to have leaked at an intermediate gasket connecting sections of the chamber, a conclusion based on the oxidation of a galvanized fastener at the leak sight and the presence of precipitate on the gasket surface. The gasketed connection did not show any signs of being loose (under tightened). Evidence of the leak appeared in the first photograph taken during the experiment. The location of the marking on the inside of the flight container indicates the leak took place while the container was lying horizontal and upside down. There was evidence of a small trickle of reactant and/or product on the payload mounting plate and a small accumulation at one of the purge port plugs. The liquid would have "run" to this location only when the payload was horizontal and upside down, which leads to the hypothesis that the leak took place during launch. The leak in the gasketed connection apparently resulted from vibration and/or g-loading. None of the gasketed connections had leaked during any testing of these chambers.

In summary, the chemical concentrations were intentionally low. At no time was the container in any danger of structural or other failure because of corrosion.

The appearance of the container was worsened because the galvanized fasteners "rusted" in the presence of an oxidizer. This "rust" contributed to the discoloration of the container and a small section of the aluminum on the payload structure.

Equipment and General Payload The entire payload was prepared in accordance with NASA NHB, 1700.7B, "Safety Policy and Requirements for Payloads Using The Space Transportation System" and with "Getaway Special Payloads, Safety Manual" as revised 12/2/83. The G-0405 payload was designed for one 2.5 ft³ canister (although NASA ultimately flew it within a 5.0 ft³ canister) and had a maximum weight of 60 pounds. The payload was self-contained and required only one twisted, shielded pair of wires as a signal cable. A detailed description of all subsystems and materials is available from the authors. The payload was purged with dry nitrogen gas before flight and sealed.

CONCLUSIONS

The experiments and the equipment designed to carry out the reactions by remote control were successful. The reactions were effected in zero gravity as expected, and the desired precipitates were formed.

The major difference in the precipitates prepared in microgravity versus those prepared on earth is that in the former the particles generally are much larger or more well-developed. Manganese dihydroxide Mn(OH)₂ is a gelatinous precipitate; the sample formed in space shows a larger, granular type of precipitate. The barium sulfate BaSO₄ precipitate particles in the space sample appear larger. Rod-like structures which are apparent in one picture of the space sample and not in those of the earth sample have an increased manganese content. Mercuric chloride HgCl₂ is a curdy precipitate; the x-ray examination revealed the particles to be crystalline in both samples, with those formed in space being larger and more well-developed than those formed on earth.

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