Heavy Water for the Savannah River Site

J. W. (Bill) Morris
William P. Bebbington, Robert G. Garvin, Mal C. Schroder,
and W. C. Scotten

Abstract

In late 1950, the supply of heavy water was recognized as a critical factor for the early startup of proposed nuclear reactors at the Savannah River Site (SRS). A new production process was demonstrated using hydrogen sulfide in a dual-temperature cycle with water to extract and concentrate heavy water from natural water. Two large plants were built and operated beginning in 1951. One was located at the Dana Plant in Indiana, and the other was at the Savannah River Site (then the Savannah River Plant). Formidable problems were resolved in control of the new process, in dealing with the corrosive hydrogen sulfide-water system, and in handling large amounts of the hazardous gas. Tonnages of heavy water produced were unprecedented at the time and were available early enough that supply was not a limiting factor in reactor startups. Both plants operated with excellent safety records and with high on-stream efficiencies. With adequate supplies of heavy water on hand and with no significant new requirements in the United States, the Dana Plant was closed in 1957. A major part of the SRP heavy water production plant was closed later in 1957-1958, and the remainder shut down in 1982.

This will be an historical saga, not a technical paper. Heavy water was a critical item for Site reactor startups, and that need was met. Between 1951 and 1982 over 7,000 tons was produced by Du Pont.

Water is a chemical compound consisting of two atoms of hydrogen and one of oxygen, designated in chemical shorthand as H_2O. Hydrogen is the smallest and simplest of all the chemical elements and was assigned an atomic mass of one. In fact, however, hydrogen in the earth's environment contains three isotopes, forms of the element that behave almost the same chemically but have different masses. Nearly all natural hydrogen does have a unit mass of one. But about 1 part in 7000, or about 140 parts per 1,000,000, has a mass of 2 and is called deuterium, symbol D. The third isotope of hydrogen has a unit mass of 3 and is called tritium. Tritium is radioactive, and its concentration is negligible in natural sources.

The term "heavy water" refers to deuterium oxide, D_2O. In contrast, natural water is called "light water" because the hydrogen in natural water is more than 99.98% mass 1. The heavy-water concentrations of natural waters do vary a bit from the normal range of 0.0148 ± 0.0002 %, but no natural enrichment is known that would be economically significant.

The production program for heavy water for the Savannah River Plant (SRP) began before the Site was chosen. Du Pont had pertinent experience with heavy water, having produced 32 tons of it for the Manhattan District in facilities at 3 ordnance plants built and operated by the Company during World War II. These large facilities used vacuum distillation of water followed by electrolysis for final concentration. When the Atomic Energy Commission (AEC) in the late 1940s undertook a large program to produce both tritium and larger amounts of plutonium, heavy water was the preferred moderator for the new nuclear reactors. Three production processes were seriously considered for the most difficult step; increasing the initial 1 part in 7000 by a factor of several hundred; vacuum distillation of water, distillation of liquid hydrogen, and exchange of liquid water with hydrogen sulfide (H_2S) gas in a dual-temperature cycle. Vacuum distillation of water was known to work but at great cost.

Hydrogen distillation offered a large separation factor but handling large quantities of liquid hydrogen had not been demonstrated. The large quantities of hydrogen needed were not readily available. Hydrogen sulfide dual-temperature exchange was feasible based on laboratory data, but the process had not been demonstrated. A critical problem in process control had been recognized but not solved, and the gas was both corrosive and very toxic. The potential advantages of the hydrogen sulfide process were so significant, however, that in 1949 the AEC asked the Girdler Corporation to design, build, and operate a pilot plant of significant scale and to design a large production facility. This program was given high priority because availability of unprecedented quantities of heavy water would be critical to the schedule for the proposed nuclear reactors. The location chosen for the pilot plant and the potential production plant for the "GS" (for Girdler sulfide) process was the site of the Wabash River Ordnance Works, which included the largest of the WW II heavy water plants. It offered some equipment that might be reused, and a large steam generating plant that could be returned to service.

When Du Pont accepted its role as prime contractor for what became the Savannah River Plant project, responsibility for heavy-water supply was included. An early review confirmed the advantages of the H_2S process if major uncertainties of toxicity, corrosion, and process control could be overcome. At this point Du Pont joined Girdler with primary responsibility for oversight of design and development activities, including operation of the pilot plant to demonstrate operability and process control. Du Pont's experience with hazardous materials gave optimism that dedicated safety procedures and equipment could handle gas toxicity, and an extensive corrosion research program was initiated within the Du Pont Engineering Research Laboratory to confirm and extend preliminary conclusions that conventional materials of construction could be used. Du Pont engineers worked with Girdler on process design and materials of construction. Girdler engineering personnel were very capable and cooperative, and this collaboration worked well. Construction of the pilot plant was nearing completion and about a dozen Du Pont people were transferred there to oversee operations. We were there on duty in late November 1950, when the Savannah River Site was announced. That heavy-water facility soon became known as the Dana Plant, named for the nearby village of Dana, Indiana.

The GS process is based on the fact that in the gas-liquid H_2S-H_2O system, deuterium is distributed better to the liquid phase at low temperature than at high. Thus, if a stream of water flows first down a cold gas-liquid multi-contact tower countercurrent to a flow of hydrogen sulfide gas, then down a similar hot tower countercurrent to that same gas, deuterium will be absorbed from the gas in the cold tower, stripped from the liquid in the hot tower, and thus concentrated at the bottom of the cold tower and the top of the hot. Portions of those concentrated streams can be withdrawn from that two-column "stage", either as product or for further concentration. The process control problem is that the liquid/gas (L/G) ratio of these countercurrent flows must be controlled more closely than conventional instrumentation allows. Deviation of the L/G from optimum, either up or down, greatly decreases productivity. The solution to the problem was devised by the late Dale F. Babcock, senior member of Du Pont's pilot-plant task force. He pointed out that the mid-column concentrations of deuterium in the hot and cold towers would be nearly equal at optimum L/G, and that the ratio of the two concentrations would be extraordinarily sensitive to variations in the L/G. Use of this principle in the pilot plan demonstrated that it solved the problem, and the ratio was later used routinely in the production facilities. Analysis was made by mass spectrometer to determine mass 18:19 (H_2O:HDO) ratio, and at higher concentrations for mass 19:20 (HDO:D_2O).

The pilot plant had been designed and built as a four-stage unit. The major uncertainties were process control, operability, and tray efficiency under process conditions. Resolving these uncertainties required only the first stage, consisting of 2 mild steel towers, each 3 feet in diameter by 110 feet tall and with 70 bubble cap trays. Auxiliary equipment included a rotary sliding vane compressor for gas circulation and centrifugal pumps for liquids, with spares in both services. A particular problem was that hydrogen sulfide and water form a solid hydrate at temperatures below 29.5ºC (80ºF) at 325 psig. The hydrate problem required that all sample lines and other small lines be heated to at least 30ºC (86ºF). Steam tracing was used for small lines, and generally electrical heating for instrument enclosures. This hydrate problem was a real aggravation for attempted pilot-plant operations during November 1950, when ambient temperatures dropped to −20ºF (-29ºC).

Shortly after pilot-plant startup, hydrogen sulfide stress corrosion cracking became painfully evident when the internal roller bearings of both the gas blower and its spare shattered into sharp, hard steel fragments. Despite this and numerous other problems, successful operation of the pilot plant was achieved beginning at about 2 p.m. on October 26, 1950, and continued for almost 300 hours before shutdown was necessitated by other mechanical difficulties. During this operation, the concept of the ratio of mid-column concentrations to indicate the critical liquid/gas flow ratio was well demonstrated. The data showed that a flow ratio near optimum was maintained from hour 100 to 140, and that directions and approximate magnitudes of needed corrections in flow ratios were clearly indicated. The data also permitted determination of average bubble cap tray efficiencies of at least 45% for the two-column system. Taken as a whole, the pilot-plant operations and data were judged adequate to justify the choice of the GS process for the production plant. The operational difficulties, however, together with the risk of loss of valuable product by high pressure leaks, led to the decision to limit that process to about 15-20% heavy water. This approximately thousandfold factor over the initial concentration of 0.014% constitutes the bulk of the total separative work and consequent cost for both facilities and energy. Vacuum distillation (DW process) would be used to bring the concentration up to about 90%, followed by batch electrolysis (E process) to achieve final, reactor-grade purity of 99.75% minimum. These two processes represented extensive industrial-scale experience, simple and straightforward process control, and little possibility for product losses. At Dana, parts of the wartime plant were used for the DW process.

The Girdler Corporation continued with engineering design and began construction of the Dana Plant production facilities. Particular attention was given to the intricacies of process control, corrosion/materials of construction, and the hazards of hydrogen sulfide. Shortly thereafter, decision was reached that an additional heavy-water plant also would be required to meet the schedules for the new nuclear reactors. That plant would be built at the Savannah River Site, along with a power plant to provide both electric power and process heat.

The R&D program on materials of construction was expanded and carried out throughout design and construction, the results being applied concurrently at both plants. Subsequent findings in the operating plants extended those experimental data. The following principles were used in construction and maintenance as early as possible:

1. Carbon steel was used for most process vessels and for heat exchanger shells and piping. Steel plate to be used for process vessels was carefully examined by ultrasonic inspection to reject any that contained fissures, voids, or laminar inclusions. Most bubble caps and trays were constructed of Type 410 stainless steel (SS). At SRP, however, towers in two of the three "buildings" were clad and caps and trays were constructed with Type 304 SS.
2. Hardness of all bolts was limited to 27 on the

Rockwell "C" scale, and imposed stresses were limited to 40,000 psi measured by extensometer as bolts were tightened.
3. Process units were to be given thorough annual inspections and hydrostatic testing.
4. Lower-than-normal industrial velocities were used in steel piping, and liquid entrainment was minimized in gas lines.
5. Stainless steel was used where high velocities were necessary (e.g., orifice plates).
6. Minimum thickness holes (small holes drilled partway through) were used to give early warning of wall thinning where erosion or entrainment was likely.
7. Metal parts in which stress or hardness was necessary, such as Bourdon tubes, springs, and instrument bellows, were isolated from hydrogen sulfide.

While the foregoing measures did not eliminate corrosion in the process plants, they did make the consequences tolerable.

Beyond the foregoing measures that were taken to contain the hydrogen sulfide, a broad program was established to deal with its inherent hazards. The material is extremely toxic, more so than hydrogen cyanide. Each of the two GS plants would contain about 800 tons of the gas under pressures up to 250-300 psig. The physiological effects of H_2S are insidious in that the gas has a foul odor of rotten eggs at initial exposure to low concentrations, but continuing exposure to higher concentrations anesthetizes the olfactory system and masks the odor. Exposure to significant quantities of the gas can quickly lead to unconsciousness, but recovery is rapid and complete if fresh air is provided quickly. To deal with these hazards, a comprehensive safety program was formulated, including the following:

1. Extensive monitoring systems were established to detect hydrogen sulfide in the air.
2. Masks with breathing air reservoirs ("Air Packs") were provided in process areas and absorbent canister masks in more distant areas. All personnel in plant areas were trained in artificial resuscitation.
3. A 400-foot-high flare stack was provided for each GS plant to vent and burn gas that had to be released. Quick-acting isolation and dump valves were provided.
4. A "buddy" system was established for the GS and gas generation plants. All personnel working in the units were extensively trained and worked in pairs. Each individual in the pair carried an air pack, and they stayed far enough apart that if one were overcome, the other could rescue him.

These measures, and constant vigilance, permitted the entire production program of heavy water to be carried out with no serious injuries from exposure to hydrogen sulfide. A few people were overcome, but all responded either to fresh air or to artificial resuscitation if necessary, and none suffered any lasting ill effects.

Engineering design for the Dana production facility proceeded with the concept developed by Girdler under its initial contract with AEC. Extraction and initial concentration of heavy water from the feed water from the Wabash River involved six GS units, each consisting of five stages of cold-hot tower systems. The first stage of each unit consisted of four cold-hot tower pairs in parallel; the second stage, one cold-hot tower pair of the same size; and subsequent three stages, towers of the same height but progressively decreasing diameters. Each tower had 70 trays and was about 120 feet tall. The first- and second-stage cold and hot towers were 11 and 12 feet in diameter, the third 6 and 6.5, the fourth 3.5 and 4, and the fifth 2.5 each. Concern for the operability and process control of the large, complex tower systems of the Dana design led to the choice of simpler independent units for the plant at the Site. It had 24 identical units, each with only 2 stages, but the second stages each had over twice as many separative trays as those in the Dana design. The second-stage SRP cold and hot towers were each built as two physical units in series and were 6.5 feet in diameter, roughly the same as stage 3 at Dana. The first stage SRP towers were the same diameters as those at Dana. The diameters of the larger towers were limited to sizes that could be transported by rail from fabrication plants scattered about the country. Fabrication of the 96 towers for Dana and 144 for Savannah River taxed the capability of the vendors of such equipment in this country during construction of the two plants. Space does not permit inclusion of photographs or flow diagrams, but each of the two large plants was quite impressive in appearance.

Each of the 24 GS units of the SRP design contained only 4 interrelated process flows, while each unit of the Dana design contained 6 times as many. Flow control problems at Dana were compounded by the much more complex interstage relationships and by the parallel first-stage arrangements. Because of these complexities, all gas process blowers and liquid circulatory pumps at Dana were equipped with spares to minimize upsets, while spare blowers and pumps were not justifiable in the simpler SRP design.

The first attempted startup of a Dana Plant GS unit occurred during the winter of 1951-52. Hydrogen sulfide gas was introduced to displace water in the first stage towers. After the system had been brought up to process conditions and flows, pressure drops in the towers were lower than expected, and anticipated buildup of heavy water was not achieved. When the unit was shut down and the towers were opened for inspection, many of the uppermost trays in the towers were found to have collapsed. Evidently, the temperature had fallen so low that solid hydrogen sulfide hydrate formed, overloading and collapsing the trays. Also, many of the slotted bubble caps on the trays were broken. The caps had been made by cold pressing, and had not been annealed. Much work and several months of delay were incurred while the column internals were removed and repaired, bubble caps and other manufactured parts were replaced by properly stress-relieved parts, startup procedures were extensively revised, and piping changes were made to accommodate the revised procedures. Such lessons learned at Dana were very painful, but the resulting findings were beneficial to both heavy-water plants. The first successful startup of a Dana GS unit was in early August 1952, and of one at Savannah River was in October of that year. All parts of both plants were in full operation by May 1953.

The Dana Plant provided the nucleus of the operating and technical staffs at Savannah River, and the two plants collaborated fully in all matters. In fact, the plants engaged in friendly but vigorous competition, especially in safety records and productivity. Each plant had been designed for a conservative production capability of 240 tons of heavy water per year. Each achieved that rate within about a year after full startup, and exceeded it by more than a factor of two within about two more years. Both plants operated consistently well after a variety of startup problems. Changes were made when indicated. In one instance, after a number of years of operation, the screwed joint of a 16-inch flange failed at SRP and within 20 minutes 46 tons of H_2S burned before it could be dumped to the flare tower. The heat carried the gases up above the surrounding towers where winds dissipated the fumes. H_2S was barely detectable at ground level, and no injuries resulted. Investigation found that poorly machined threads and warping of the flange by normal bolt loads caused the failure. Thereafter, all 16-inch and 12-inch screwed flanges were replaced by welded flanges.

Process control using ratios of mid-column concentrations worked well at both plants. The sensitivity of that ratio was so high that a change of flow rate as small as 0.5% could be detected and correction could be made. Over the course of time and with instrumentation steadily improving with experience, sampling frequencies were considerably reduced.

The simpler design of the GS process at SRP led to lower down time and higher operating efficiency there. The SRP GS units were out of productive operation only about 2% of the time, most of which was for the required annual overhaul, inspection, and hydrostatic test. The more complex Dana units, in contrast, required about 17 days, or about 4-1/2% of annual operating time. Also, at Dana these procedures were prohibitively difficult during the cold winters, whereas at SRP such work was possible year-round. Thus, the productivity at SRP was greater than at Dana.

The production capabilities of the two heavy-water plants had been planned to meet the needs of the new reactors at the Savannah River Site without the heavy-water supply becoming a limiting factor. That goal was accomplished, and with a large reserve on hand, the Dana Plant was closed early in 1957. Although the facility had operated satisfactorily, major replacement of corroded Type 410 stainless steel trays would have been needed soon, and operating costs were higher than those at Savannah River. In the course of time, the Dana facilities were dismantled and sold.

At Savannah River, one of the three GS buildings, the one with unclad towers and Type 410 SS trays, was shut down on October 4, 1957. Corrosion was much more severe than in the other two buildings with clad towers and Type 304 SS trays. Soon afterward, calculations showed and a plant test demonstrated that with only two GS buildings operating, the E Plant could be shut down, and final product concentration was achieved in the DW Plant without significant loss in production. Operation without the E Plant produced considerable cost savings.

In October 1958, one of the remaining two GS buildings was shut down as inventories mounted. Also, to reconcentrate heavy water diluted during reactor operations, and to avoid tritium contamination of virgin heavy-water product, 3 of the 10 DW towers were isolated for such “rework” in 1957 and a fourth was added in 1960. Ultimately, the need for new heavy water decreased, and inventories rose to the point that this remaining production unit was shut down on January 8, 1982. At that time only three reactors were in service, their losses of heavy water were small, a large inventory was on hand, and continuing production was not justified. The “SRS News” of December 1995 carried a story and photograph of the dismantlement and removal of the flare stack, the GS process facility, the hydrogen sulfide generation plant, and interconnecting piping. Thus were removed the last visible indications of the production program for heavy water for the Savannah River Site.

Several corollary activities of the production program that warrant mention were carried out by or for the AEC and its successor agencies. Considerable amounts of heavy water were sold to scientific organizations for research, and by 1964, almost a thousand tons had been sold and exported to other countries. Several countries seriously considered heavy-water-moderated reactors for electric power generation, and permission was given for some of them to send visitors to the SRP production facility to obtain first-hand information. Canada in particular, having built a unique facility that produced a significant tonnage of heavy water for the Manhattan District during World War II, established a major program for producing, using, and exporting heavy-water-moderated power reactors. From 1965 to 1973, the Canadians built three different large production plants based on the GS process. The first suffered major deficiencies in design, and Du Pont engineers were called upon to help in devising remedies. The plant was ultimately rebuilt completely. Later plants were successfully built and operated after Canadian personnel were trained at SRP. Du Pont engineers were assigned to assist in startup and initial operations of these Canadian plants. Over time, these plants produced considerably more heavy water than had the U.S. plants. But as in the U.S., eventually decreased demands and increasing inventories led to shutdowns. As of this writing, the last of the Canadian plants are being dismantled.

Last but not least, major credit for the successful production of heavy water at both Dana and Savannah River goes to the people who oversaw operations and the maintenance work, and in general made the production wheels go around. They seldom had their names attached to technical papers, but without them the plants could not have operated safely or successfully. Their work in dealing with hazardous gas under high pressure, their dependence on the buddy system, and the stressful work of annual overhauls melded them into cohesive, effective units.

In summary, heavy water was produced for the Savannah River Site in two major production facilities designed, built, and operated under Du Pont supervision. Over 6000 tons were produced at Savannah River, and an estimated 1,200 to 1,500 tons at the Dana Plant. The plants operated safely despite handling unprecedented quantities of extremely toxic gas, and their product was available in time for the demanding schedule for reactor startups.

Biographies

J. W. Morris

J. W. (Bill) Morris earned B.S., M.S., and Ph.D. degrees in chemical engineering at the University of Texas at Austin. He then joined Du Pont in Wilmington, Delaware, but shortly was assigned to Du Pont's work for the Manhattan Project. After training at Oak Ridge, he went to Hanford, heading radiation protection for the final purification, concentration, and shipment of the product, plutonium. In late 1945, he returned to Du Pont's Grasselli Chemicals Department, where he served in Wilmington and in Cleveland, Ohio. In 1950, he joined Du Pont's return to nuclear matters, first in heavy water production at the Dana Plant in Indiana, where he became Technical Superintendent. In 1953, he came to the Savannah River Laboratory in South Carolina. There he was successively Director for separations R&D; for reactor engineering and materials R&D; and for University Relations. After a final assignment in environmental engineering, he retired at the end of 1983.

W. P. Bebbington

William P. Bebbington earned a Ph.D. degree in chemical engineering at Cornell University in 1940. In addition to his heavy-water experience during World War II, he held Du Pont assignments in high-pressure synthesis of ammonia, methanol, and polyethylene. As Du Pont began work on the Savannah River Plant in 1950, he headed the plant's Heavy Water Technology Section and later held management assignments in research and development. During Mr. Bebbington's last 12 years at SRP, he was General Superintendent of the Works Technical Department with responsibility for all aspects of the nuclear fuel cycle and also for radiation protection and environmental monitoring and protection. He has published technical papers on the production of heavy water, nuclear criticality safety, and environmental effects. He is the author of a *Scientific American* article on reprocessing of reactor fuels and a booklet on radioactive wastes that has been widely distributed by the American Institute of Chemical Engineers. He is a fellow of the American Institute of Chemical Engineers and in 1979 received the AICHE's Robert E. Wilson Award in Nuclear Chemical Engineering.

R. G. Garvin

Robert G. Garvin earned a B.A. degree and a B.S. in chemical engineering degree at Rice University and a M.S. in chemical engineering from North Carolina State University. He joined Du Pont at the Savannah River Plant in 1957 and served in a number of technical and management positions, including 10 years with heavy water operations, until his retirement in 1991. In 1969, he and the late Charles Gresham served as technical and production advisors respectively at the heavy-water plant in Port Hawkesbury, Nova Scotia, during startup and initial operation. From 1970 to 1973, he served as SRP liaison at the Bruce Heavy Water Plant in Douglas Point, Ontario, during the final stages of construction and startup.

M. C. Schroder

M. C. (Mal) Schroder earned a B.S. degree in chemical engineering from Louisiana State University in 1950 and joined Du Pont in Wilmington in 1951. Shortly thereafter he was called to serve in the Korean conflict. He returned to the Du Pont Construction Division at Pensacola, Florida, in 1953. The next year he transferred to the Savannah River Plant where he was assigned to the Separations Technology Group. In 1960, he was assigned as a supervisor in the Heavy Water Technology Group, and he later became superintendent of the Heavy Water Production Group. When heavy water production was curtailed he was transferred to other positions in Plant Maintenance, Defense Waste Planning, and design liaison and plant startup preparations for the Defense Waste Processing Facility. He retired at the end of 1986, but was called back as a consultant for the design of a new production reactor in 1991-92.

W. C. Scotten

W. C. Scotten earned a B.S. degree in 1943, and a Master of Science degree in 1947 in chemical engineering from the University of Missouri-Columbia. After joining the Pure Oil Co. in 1943, Mr. Scotten joined the Naval Reserve from 1944 to 1946. He subsequently worked for Du Pont at the following locations: Du Pont Grasselli, Experimental Station, Wilmington, 1947-51; Du Pont AED Works Technical, Dana, 1951-52; Du Pont AED, Works Technical, SRP, 1952-1982.