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Stable Isotope Separation
AEC Research and Development Report

PRODUCTION OF HEAVY WATER
SAVANNAH RIVER AND DANA PLANTS
TECHNICAL MANUAL

July 1959

E. I. du Pont de Nemours & Co.
Savannah River Laboratory
Aiken, South Carolina

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STABLE-ISOTOPE SEPARATION
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PRODUCTION OF HEAVY WATER
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TECHNICAL MANUAL

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J. W. Morris, Director
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ABSTRACT

This manual is a summary of the basic technical information that pertains to processes that are used at the Dana and Savannah River Plants for the production of heavy water. The manual is intended primarily for plant operating and technical personnel and was prepared to supplement and provide technical support for detailed operating procedures.

The introductory sections of the manual contain some background information on the history, uses, available processes, and analytical procedures for heavy water. They also include a general comparison of the design and performance of the two plants and an analysis of their differences.

In subsequent sections, the technology of the heavy water separation processes used, namely hydrogen sulfide exchange, distillation of water, and electrolysis is discussed in detail. The manufacture and storage of hydrogen sulfide gas and the process water treatment facilities are also discussed.

FOREWORD

This report is a summary of the technology used in the production of heavy water in the Dana and Savannah River Plants, as operated by du Pont for the Atomic Energy Commission. As such, the report is largely a revision and consolidation of five technical manuals written as guides for the operation of the Dana Plant. The titles and authors of the Dana manuals, which were issued originally as *S cret* documents, are listed below.

Dana Plant Technical Manual:

- Part I - Introduction and GS Process -
W. P. Bebbington and W. R. Keller
- Part II - DW Process -
V. R. Thayer, A. F. Fritzlen, and C. W. Stahl
- Part III - E Process -
W. P. Bebbington, C. W. Stahl, and F. E. Warren
- Part IV - Gas Generation -
W. P. Bebbington and C. B. Buford, Jr.
- Part V - Treatment of Feed Water for GS Process -
J. A. Lutz

No separate technical manuals were written for the Savannah River heavy water plant; the technology used there was sufficiently similar to that used at Dana to make separate manuals unnecessary. In this present report the technology of both sites is included, revised to include process changes made as the result of operating experience. The original Dana manuals are now obsolete.

Compilation of this report was started in 1957, at the time the Dana Plant was being shut down because its capacity was no longer needed. Since the purpose of the report is to describe as clearly as possible the technologies and facilities of the two plants as built and operated, the Dana material is presented in the present tense.

Final completion and issuance of this report was delayed because of temporary restraining orders which continued during the pendency of Federal court action. This court action was dismissed on July 23, 1959, by the U. S. District Court for the District of Columbia.

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PRODUCTION OF HEAVY WATER
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INTRODUCTION

Facilities have been built and operated to produce heavy water (deuterium oxide, D_2O), of high isotopic and chemical purity, by separation from natural water.

Two plants were built for this purpose, one at Dana, Indiana (Dana Plant) and one near Aiken, South Carolina (Savannah River Plant). The heavy water facilities at the Savannah River Plant are a part of the over-all plant which includes various nuclear operations.

NATURE AND USE OF HEAVY WATER

Deuterium is one of the three known isotopes of hydrogen. Natural water, other hydrogen-containing compounds, and ordinary hydrogen gas contain mainly the isotope having an atomic weight of 1.0. Deuterium, the second isotope, has an atomic weight of 2.0, and tritium, the third isotope, has an atomic weight of 3.0. As is the rule with isotopes, these three types of atom share the same atomic number, 1, and have nearly identical chemical properties.

Generally, in chemical work, the term "hydrogen" is taken to mean the naturally occurring mixture of isotopes of this element, and "water" means the mixed oxides of the element. In discussions of separations of the isotopic forms, the term "hydrogen" is generally assigned to the most abundant isotope having atomic weight 1.0. "Protium" has been proposed as a specific name for this isotope, but has not gained wide acceptance. The term "light water" is applied to the oxide of the light isotope having a molecular weight of 18, and "heavy water" is applied to deuterium oxide, having a molecular weight of 20.

Heavy water is used principally as a moderator in nuclear reactors. Its value as a moderator is due to the superior ability of deuterium atoms to absorb energy from neutrons which collide with them, without at the same time "capturing" or uniting with too many of these neutrons.⁽¹⁾ In the form of heavy water, the attractive nuclear properties of deuterium are provided in a convenient physical and chemical state.

About 0.015 mol % of the hydrogen in natural water is deuterium, which at this low concentration, exists in solution as HDO^* . The

* For a discussion of the molecular forms in which deuterium exists in water of various concentrations see Appendix A.

ratio of deuterium to hydrogen varies only slightly among the many sources of the element and its compounds. Diligent search has revealed no natural source of deuterium that is sufficiently above normal concentration to be economically significant.⁽²⁾

Tritium is a radioactive isotope of hydrogen. It occurs naturally only in extremely small concentrations.

ISOTOPE SEPARATION

Since all of the isotopes of an element have essentially the same chemical properties, common chemical methods of separation are generally not applicable. The several isotopes of an element, and their related compounds do, however, show some differences in physical properties. Also, although the chemical properties of all the isotopes of an element are qualitatively the same, there are quantitative differences. The chemical differences are generally in reaction rates, reaction equilibrium constants, and the like. Isotopic separations can be based on these differences. Fortunately, the physical and chemical differences between hydrogen and deuterium, because of their twofold mass ratio, are greater than for pairs of isotopes having lower mass ratios. The small percentage of deuterium in nature, however, makes the recovery of large quantities of heavy water a difficult and costly undertaking.

METHODS OF SEPARATION OF HEAVY WATER OR HEAVY HYDROGEN

Several methods that have been applied to or proposed for the large-scale production of deuterium or heavy water are outlined in Table I.*

TABLE I

Methods of Separation of Heavy Water or Heavy Hydrogen

<u>Method</u>	<u>Advantages</u>	<u>Disadvantages</u>
Distillation of hydrogen	Large difference in volatility of H vs. D, hence ease of separation	Involves large-scale distillation of liquid hydrogen for which commercial technology is not fully developed; limited commercial sources of hydrogen gas
Fractional diffusion, hydrogen gas	Good separation factor; simple equipment	High energy requirement and large investment in gas compressors
Electrolysis of water (hereafter called the E process)	Good separation factor	Very high electric energy consumption

* There are now many discussions of heavy water processes in the AEC project and open literature. References to a number of these are included in the Bibliography.

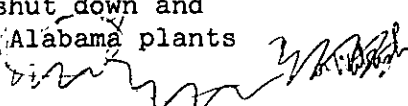
<u>Method</u>	<u>Advantages</u>	<u>Disadvantages</u>
Distillation of water, (hereafter called the DW process)	Simple equipment and operation	High thermal energy requirement and low separation factor
Gas-liquid exchange processes		
H ₂ S-H ₂ O, dual temperature (hereafter called the GS process)	Good separation factor with moderate energy and equipment requirements; no catalyst	Toxicity of H ₂ S; corrosive nature of the H ₂ S-H ₂ O system
H ₂ -NH ₃ , dual temperature	Good separation factor; reasonable equipment and energy requirement; simple homogeneous catalyst	Requires secondary source of D since NH ₃ supply is limited; process not developed for commercial application
H ₂ -H ₂ O, single temperature	Good separation factor; atmospheric pressure operation	Vapor-phase exchange reaction over catalyst; applicable only where supply of pure hydrogen is available (as at Trail, B.C.)

HISTORY OF HEAVY WATER MANUFACTURE

Deuterium was first isolated in concentration sufficient for positive identification by Urey and his co-workers at Columbia University in 1931. This first rough separation was by fractional evaporation of liquid hydrogen. Subsequently, G. N. Lewis at the University of California concentrated a large quantity of water to a small amount of nearly pure D₂O by electrolysis. The heavy isotope of hydrogen was of great interest to research workers as a tracer in biochemical processes and chemical reactions as well as to scientists who were studying the comparative properties of the two isotopes and their compounds. The demand for heavy water and deuterium was sufficient to justify their commercial production on a small scale, usually as byproducts of operations that were already producing hydrogen and oxygen electrolytically. The Stuart Oxygen Company in California was such a producer in this country, as were some of the firms operating electrolytic hydrogen plants in Norway.

By 1940 sufficient interest in heavy water as a neutron moderator had been aroused to initiate a research and development program at Columbia that was aimed at a practical large-scale process for its separation. This work spread to many other university and industrial research laboratories, and led to the preliminary development of most of the methods of separation summarized in Table I. The outcome of

this program (initiated by the Office of Scientific Research and Development, and carried to conclusion by the Manhattan District, Corps of Engineers) was the construction and operation of a unit at the Trail, British Columbia plant of Consolidated Mining and Smelting Company and of plants at the du Pont-operated Morgantown, Alabama, and Wabash River Ordnance Works (WROW). The former used a combined hydrogen-water exchange and electrolytic process operated as an auxiliary to the C.M.&S. electrolytic hydrogen plant, and the latter used vacuum distillation of water, followed by an electrolytic process for final concentration.⁽³⁾ The total capacity of these facilities was, however, insignificant compared to those described in this Manual.

The heavy water program of 1940-45 was initiated before the demonstration of any kind of nuclear reactor. Before construction of the du Pont heavy water facilities was started, however, the first graphite "pile" at Chicago had operated successfully. The production of heavy water from 1943 to 1945 thus became part of a secondary development program rather than part of the principal effort. By the end of the war sufficient heavy water had been produced for the experimental reactors that were planned, and the du Pont units were shut down and placed in standby condition. (Later the Morgantown and Alabama plants were scrapped.) The C.M.&S. plant continued operation. 

A small portion of the original WROW distillation plant is being used for intermediate concentration of heavy water and for deaeration of GS feed water at the Dana Plant. Some equipment from the Morgantown electrolytic plant is similarly being used for the final concentration of heavy water in the Dana E plant, which is essentially an enlarged version of the Morgantown installation. The Dana cells, incidentally, vary only in details from those that were originally used by the Stuart Oxygen Company.

Development work on heavy water processes other than those used by du Pont and at Trail was ~~abandoned~~^{interrupted} in 1943 because of scarcity of materials and technical manpower, and waning interest in the material for the Manhattan District project. Work on the GS process at Columbia University had been carried through laboratory-scale tests and some corrosion research had been done, but semiworks demonstrations of the process, though carried through planning and design stages, were never completed.

SELECTION OF PROCESSES FOR THE AEC PROGRAM

AEC CONTRACTS WITH THE GIRDLER CORPORATION AND HYDROCARBON RESEARCH, INC.

During 1949, because of renewed interest in heavy water reactors, the Atomic Energy Commission authorized further study of the hydrogen distillation process and the GS process, both of which, if workable, should be less costly than water distillation.

The Hydrocarbon Research Corporation undertook studies of hydrogen distillation. These studies resulted in plant designs⁽⁴⁾ that were based on essentially the same process information that was available in 1942. Experience of Hydrocarbon Research and others, with large-scale liquefaction of air between 1942 and 1950, was helpful with regard to equipment design. There had been by 1950, however, no actual demonstration of the workability of the process design as proposed.

The Girdler Corporation was authorized to design, construct, and operate a pilot plant to demonstrate the GS process, and also to prepare designs for a large plant.

THE DU PONT SURVEY

In June 1950, the Atomic Energy Commission requested that the du Pont Company study certain phases of the atomic energy program, including heavy water production, and recommend a course of action.

The du Pont recommendations, which were adopted, were that the pilot plant program on the GS process be expedited, that part of the anticipated heavy water requirements be provided by designing and constructing production units employing the GS process for primary concentration, followed by distillation and electrolysis, and that, pending results from the GS pilot plant, designs be prepared for possible use of the water distillation process.

The GS pilot plant was subsequently operated to prove the feasibility of the GS process. Although evidence of corrosion was disquieting, the decision to rely on the GS process for primary separation of D_2O was made firm, and work on water and hydrogen distillation was discontinued.

REASON FOR CHOICE OF GS PROCESS

The decision to use the GS process was based on the following general conclusions:

1. The water distillation process, though most completely developed and most dependable, was high in capital cost and very high in thermal energy requirement compared to the alternatives.
2. The hydrogen distillation process was reasonable in operating cost, but certain important items of technology lacked development. The adequacy of hydrogen supply was questionable, and the sources were scattered. The determining conclusion was that the hydrogen distillation units could not be completed in time to meet the scheduled need for heavy water.

3. The GS process, while lacking a desirable degree of confirmation from the pilot plant, appeared to be feasible, with lower capital and operating costs than the water distillation process.

STAGING AND FINAL CONCENTRATION

The D₂O content of natural water is about one part in 7,000 and the amount that can be economically separated is no more than about one part in 30,000. Hence, immense quantities of water are required for a large heavy water plant, and the equipment through which this water is handled must be very large. By appropriate arrangements of the equipment "staging", however, the quantities of materials that are handled and the size of the equipment may be reduced about in proportion to the increase in concentration of heavy water through the plant. Energy consumption and operating cost may be reduced similarly. In a plant that is staged in this manner almost all of the capital and operating costs are associated with the first hundredfold concentration (from 0.015 to about 2%) of the heavy water. The staging may be done with any of the possible heavy water processes, or the process may be changed from stage to stage.

The value of the heavy water increases with its concentration and because of the staging discussed above, the processing costs decrease. Accordingly, in the final concentration to essentially pure heavy water, simplicity and dependability of operation are very important and the inherent economy of the process becomes less significant.

The processes for final concentration of heavy water at the Dana and Savannah River Plants were chosen on the basis of the above considerations. Advantage was taken of the inherent economy of the GS process for the extraction of D₂O from natural water and its concentration to about 15%. It was recognized, however, that the GS process was vulnerable to losses through leaks and process upsets, so the DW process (vacuum distillation) was selected for concentration from 15 to about 90%, and the E process (electrolysis) for final concentration to 99.8% D₂O. The DW process requires virtually no operating supervision and is practically immune to loss of product. The E process is particularly well suited to the final adjustment of concentration since it is a batch process with high separation factor, and the current that must be passed through the cells to achieve a desired concentration may be accurately predicted.

About 96% of the investment and 93% of the operating cost of the Dana or Savannah River heavy water plants is associated with the production of 15% D₂O in the GS process. The remaining costs are contributed by the DW and E processes.

SUMMARY

The Dana and Savannah River heavy water plants are of similar design and of approximately the same capacity. The plants were built during 1951 and 1952. The Dana Plant began operation early in 1952 and the Savannah River Plant about six months later. Both of the plants have operated dependably and efficiently to produce heavy water at considerably above their design capacity. The following section of this Manual is a summary of the essential features of the two plants and of their operating performance.

Figures 1 and 2 are general views of the Dana and Savannah River heavy water plants.

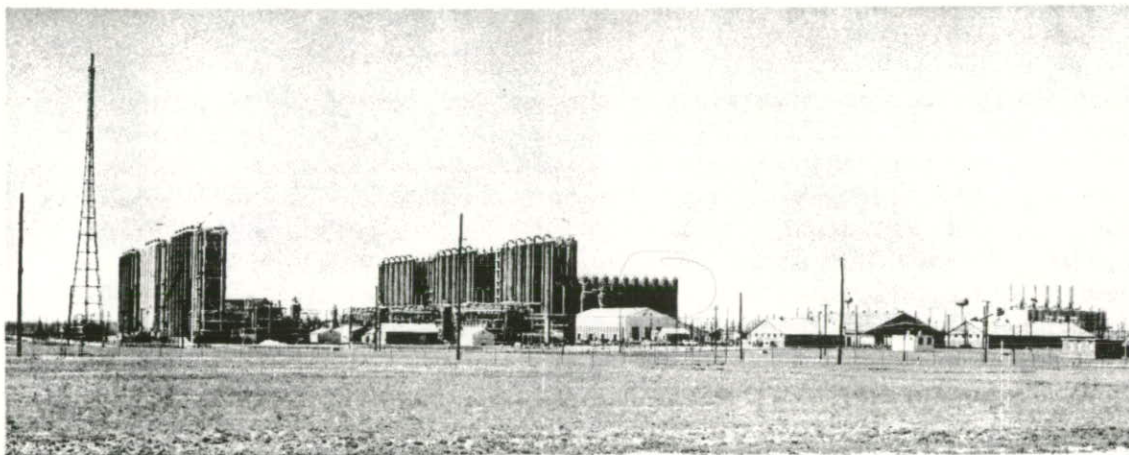


FIGURE 1 - GENERAL VIEW OF THE DANA PLANT

Prominent features are, from left to right: flare tower, south row of three GS units, control buildings, north row of three GS units, DW towers, service buildings, power house.

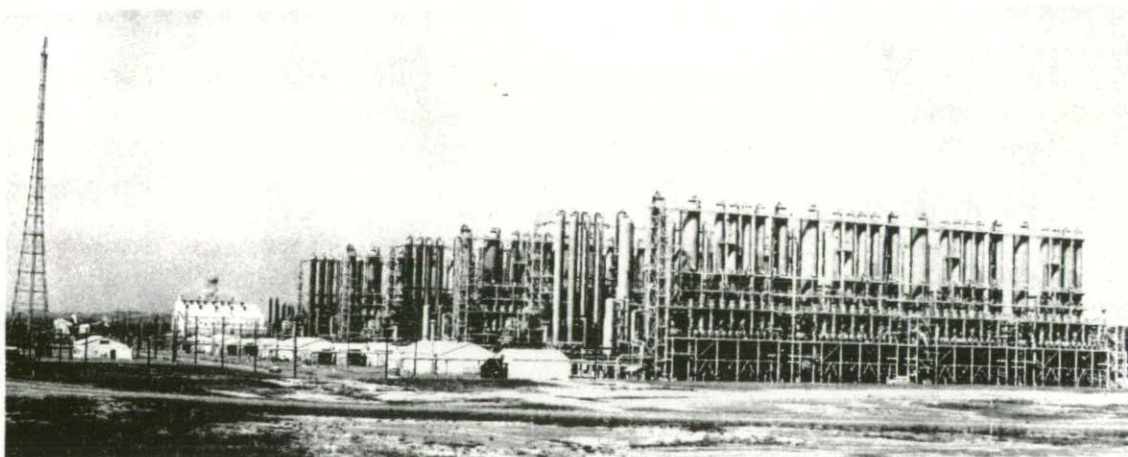


FIGURE 2 - GENERAL VIEW OF THE SAVANNAH RIVER HEAVY WATER PLANT

Prominent features are, from left to right: flare tower, power house, DW towers (in distance) GS control buildings, six rows of four GS units.

GS PROCESS

The basic element of the GS process is a pair of gas-liquid contacting towers, one of which operates at 30 to 40°C (the cold tower) and the other at 120 to 140°C (the hot tower). Water passes downward through the cold tower and then through the hot tower, countercurrent to H₂S gas at about 275 pounds per square inch gage pressure. The H₂S gas is circulated by a centrifugal blower which pumps gas from the top of the cold tower to the base of the hot tower. The water is progressively enriched in D₂O as it flows through the cold tower, is progressively depleted as it flows through the hot tower and leaves the hot tower at a concentration lower than that at which it entered the system. Thus D₂O builds up in the system, and can be withdrawn as an enriched fraction from the base of the cold tower (or top of the hot tower).

In the GS process as operated at Dana and Savannah River, natural water (containing 0.015% D₂O) is fed to the top of the cold tower, an enriched fraction containing about 0.06% D₂O is withdrawn from the bottom of the cold tower and circulated through the second stage, and depleted water containing 0.012 to 0.013% D₂O leaves the system from the base of the first-stage hot tower. The second stage consists of a pair of hot and cold towers smaller in cross-sectional area than the first stage, the reduction in area reflecting the enrichment achieved in the first stage. The cold enriched liquid from the first stage passes in turn through the second-stage cold and hot towers and returns to join the liquid stream entering the first-stage hot tower. A fraction of the hot gas leaving the first-stage hot tower is similarly circulated in turn through the second-stage hot and cold towers rejoining the first-stage flow at the base of the first-stage cold tower.

In the above fashion the complete GS unit is made up of several tower pairs in a series (or series-parallel) cascade, appropriately sized in accordance with the successive enrichment ratios. The number of elements in series (number of stages) is fixed by the over-all enrichment that is to be achieved in the cascade.

GS EQUIPMENT AT DANA

A GS cascade at Dana consists of five stages, each designed for an enrichment ratio of four. The over-all enrichment ratio is then four to the fifth power (about 1,000). With feed of 0.015%, product is therefore about 15% D₂O.

The first stage consists of four cold towers in parallel, paired with four hot towers in parallel. The cold towers are 11 feet in diameter; the hot towers 12 feet. Each tower contains 70 bubble cap plates.

The second stage has one cold tower (11 feet in diameter) and one hot tower (12 feet in diameter).

The third, fourth, and fifth stages consist of single hot tower - cold tower pairs of successively decreasing diameters, about, 6-1/2, 4, and 2-1/2 feet, respectively.

A Dana GS unit thus contains 16 towers, and there are a total of six such units. The over-all arrangement of a Dana GS unit, including towers, blowers, heat exchangers, pumps, and other auxiliaries is shown in the process flow diagram, Figure 20, and in a general view of a Dana unit, Figure 3.

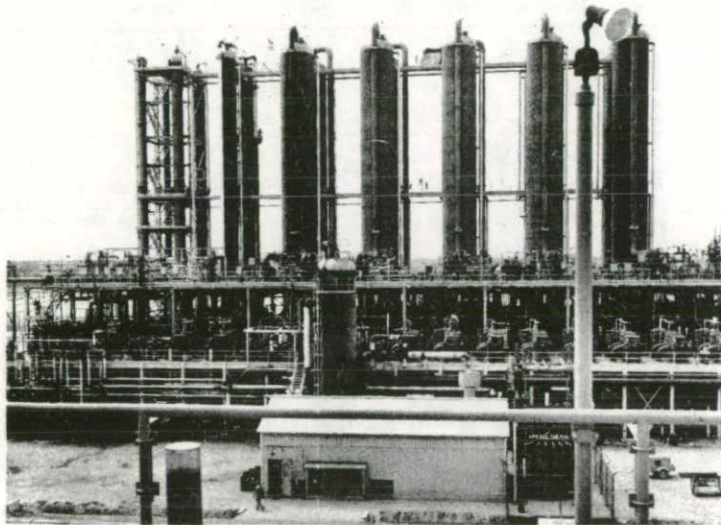


FIGURE 3 - GENERAL VIEW OF A DANA GS UNIT

Main GS towers are in background, cold towers of each pair nearly hidden behind the hot towers. From right to left are four first stage pairs; second, third, fourth, and fifth stage pairs. The heat exchangers are visible at the lowest platform level in middle distance. The short tower in foreground is the waste stripper. The building is the electrical switch-gear room.

GS EQUIPMENT AT SAVANNAH RIVER

A GS unit at Savannah River is arranged in two stages. An enrichment ratio of four to five is produced by the first stage, as at Dana, but the second stage accomplishes the necessary remaining enrichment of 200- to 250-fold.

The first stage consists of one cold tower 11 feet in diameter and one hot tower 12 feet in diameter. Each tower contains 70 plates.

The second stage consists of two cold towers in series, and two hot towers in series. The second-stage cold towers contain a total of

180 plates, and the hot towers a total of 140 plates. All four towers are 6-1/2 feet in diameter.

The GS plant at Savannah River is made up of 24 of the above units. The design capacity of a Savannah River unit is one-fourth that of the larger series-parallel cascade used at Dana. Thus the 24 small units at Savannah River have the same design capacity as the 6 large units at Dana.

Figure 4 is a view of a "wing" of four SRP GS units. This wing is equivalent in design capacity to a Dana unit.

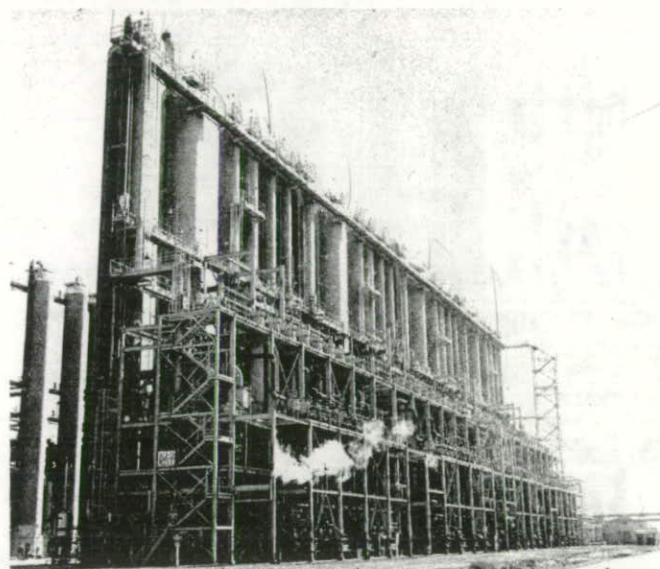


FIGURE 4 - VIEW OF A WING OF FOUR GS UNITS AT SRP

The principal towers, in order from left to right are: First-stage cold, first-stage hot, two second-stage hot, two second-stage cold; repeated four times. In front of the towers with top heads at the second main platform are the gas coolers; in front of these, with heads at the level of the first main platform are the liquid heat exchangers. A second wing of four units is partially visible in the background.

COMPARISON OF THE DESIGNS AND OPERATING CHARACTERISTICS OF THE DANA AND SAVANNAH RIVER GS UNITS

The most important difference between the Dana and Savannah River GS units is in the first stage. Operation of the four cold towers and four hot towers in parallel at Dana involves complexities of flow control that are absent in the Savannah River arrangement. The ratios of gas flows to liquid flows in the GS units are extremely critical and slight deviations from optimum in either direction cause serious reduction in efficiency. In the Dana first stage, flow ratios must be set separately in each of the eight first-stage towers. However, while the liquid flow to each hot tower must be set separately, these flows are not independent since the total flow to the hot towers must equal the total flow from the cold towers.

Operation of the Dana first-stage heat recovery system, consisting of eight parallel banks of three heat exchangers operating in series is also more complex than the Savannah River design. Water is condensed from the gas phase in the shells of these exchangers, collected and pumped to the top of the hot towers. Maintenance of condensate liquid seals in each exchanger bank is a problem in design of parallel-series exchanger pressure gradients. Formation of solid H_2S hydrate in the coldest exchanger of each bank also adds to the problem and necessitates careful control of the cooling water temperature entering the cold exchangers.

Despite complication in control of flow ratios and heat-recovery systems, the Dana GS units have operated dependably and well. The Savannah River unit is, however, inherently simpler and easier to control. While both the Dana and Savannah River GS plants represent operable designs, it is nevertheless worthwhile pointing out the significance of some of the more important differences. These are summarized in the following paragraphs:

TOWER VOLUME

The cascade at Savannah River is less nearly ideal in design in that there is only one step down in stage size (that between the first and second stage), as compared to four steps down for the Dana cascade. The Savannah River design has fewer contacting plates in series, but more total plate area, and consequently more tower volume. This means higher investment, although the tower cost is partly compensated for by reductions in cost due to simplicity in piping and auxiliaries. The Savannah cascade, excluding power house and miscellaneous facilities, is estimated to cost about 5% more than the Dana design for the same nominal capacity.

PRODUCT INVENTORY IN CASCADE

The heavy water content of the process water held up in the Savannah GS plant is two to three times that held in the Dana plant. In neither case, however, is the cost of the material that is in process large enough to be significant.

MAINTENANCE

Arrangement of the Savannah GS equipment in 24 separate units is favorable to plant maintenance, since equipment outage ordinarily affects only a small fraction of the total plant capacity. Hydrostatic tests, inspections, and overhaul are carried out on a continuous routine schedule, with units removed from service one at a time. The performance of pumps and blowers is sufficiently dependable that satisfactory continuity of operation can be maintained without installed spare units. It is not unusual for a GS unit at Savannah River to operate for an entire year without shutdown because of mechanical failure.

The 24 Savannah River units are shut down one at a time for annual overhaul and test. The overhaul and test program extends throughout the year and can be handled as a steady work load by a relatively small maintenance force.

At Dana the six large units are given inspections, hydrostatic tests, and overhaul on a campaign basis, one unit at a time over a period of three or four months. The relatively large fraction of the plant thus out of service during overhaul reduces the attainable "time on stream" at Dana by about 4% as compared to Savannah River.

At Dana all pumps and blowers beyond the first stage are installed in pairs (one operating and one spare) to ensure against outage of an entire unit in case of failure.

PROCESS CONTROL

The smaller, simpler Savannah River GS unit is easier to put "on stream" and operating control is more straightforward than it is for the Dana unit. This ease of control has contributed to a higher production rate, particularly during the first year of operation.

MATERIALS OF CONSTRUCTION FOR THE GS PROCESS

The success of the GS process has been very largely due to research and development that defined the effect of H_2S on practicable materials of construction. Concurrent with the design and construction of the two plants, a major program of corrosion research was carried out. The results of this research were applied as they were obtained, so that the Savannah River plant has the advantage of a somewhat better choice of materials than Dana.

The important aspects of the effects of hydrogen sulfide on steels are summarized below:

1. Carbon steel is corroded by H_2S in water, but the iron sulfide that is formed acts as a protective coating so that corrosion, although very rapid at first, drops to a penetration rate of less than 0.1 mil per year after about 2000 hours of exposure. If however, erosion prevents the formation of the sulfide coating, the corrosion rate remains very high. Hence for the GS process, carbon steel may be used only for equipment that is not subject to highly turbulent water flow or to spray impingement. In practice, carbon steel is satisfactory for tower shells, heat-exchanger shells (if nozzle entrances are protected), tanks, and most process piping.

2. A portion of the hydrogen that is formed by the reaction of H_2S with steel diffuses into and through the metal. This diffusion gives rise to the most troublesome effects of corrosion, stress corrosion cracking and blistering. The hydrogen, apparently, in the

atomic state, diffuses readily through the crystal lattice of steel and combines to form molecular hydrogen only at surfaces of discontinuities.

The presence of atomic hydrogen from the corrosion reaction seriously reduces the strength of hard, high strength steels or of steels having high residual stresses from cold working or welding. The effect is most pronounced and important with the high strength steels used for flange bolts and with hardened steels in springs and roller bearings. The effect of H_2S on the strength of bolts is shown in Figure 22, page 75.

Blistering is a potentially important problem in the carbon steel plates that form the walls of process pressure vessels. Any discontinuities in these plates such as voids, laminations or nonmetallic inclusions can serve as loci for the combination and collection as molecular hydrogen of any atomic hydrogen that has diffused into the steel. The hydrogen so formed can apparently generate virtually any pressure that is necessary to create space for itself. If there are sizeable voids or laminations present in the steel plate these will be enlarged by the hydrogen into blisters.

3. No corrosion inhibitors are known that are effective, have suitable physical properties, and are available at tolerable cost for use in the process. Early scouting tests indicated that ammonia or amines might be effective in inhibiting the reaction between iron and H_2S . A number of these corrosion inhibitors were tried in the Dana Pilot Plant. The over-all effect of the amines was detrimental, however, since they acted as de-scaling agents for the protective sulfide scale and did not in themselves provide an equivalent protection. The amines caused great trouble in the Dana Pilot Plant through plugging of lines with sulfide scale.

Corrosion and its effects have been kept under control by the following measures:

1. Where possible, low velocities are maintained in piping and vessels.
2. Liquid entrainment is avoided in gas lines.
3. Where high velocities are unavoidable, as in control valves and through bubble cap trays and heat exchanger tubes, stainless steel is used. AISI, Type 316, is preferred. Type 410 steel is unsuitable, being very susceptible to attack with the formation of heavy, loose scale.
4. Hardness in bolts is limited to 27 on the Rockwell C hardness scale and stresses (by measurement) are limited to 40,000 psi.

5. To ensure freedom from fissures and voids, steel plate that is to be used for process vessels is carefully selected by ultrasonic inspection.

6. Instrument bellows, bourdon tubes, and springs are isolated from contact with H_2S .

7. Liberal use is made of minimum-thickness holes at locations where erosion is to be anticipated. These holes, drilled about halfway through the pipe wall from the outside, give warning of serious penetration.

8. The units are subjected to thorough annual inspections and hydrostatic tests.

The ferrous metals, carbon and stainless steels, are used for all important process applications except the impellers of the centrifugal blowers used to circulate gas. These impellers are large in diameter and operate at high speed, and for these reasons are made of an aluminum alloy. The corrosion resistance of aluminum in this service is adequate so long as the gas is reasonably free from entrained water.

Corrosion has not been a serious obstacle in keeping plant operating time at 96 to 98%. Much, however, has been learned about this problem in operation of the plants. In the early operation of Dana, carbon steel heat exchanger tubes and control valve bodies proved to be entirely unsuitable. Type 410 stainless steel trays and bubble caps have corroded to the extent that they require replacement after about four to five years. The general attack on carbon steel piping and vessel walls has been inappreciable. There have been a fairly large number of instances of the failure of bolts because of stress corrosion cracking, and as the result of these failures the specified hardness for these bolts has been reduced to a maximum of R_c 27 and the permissible stress has been reduced to 40,000 psi. Under these conditions, no failures occur. There have been no serious instances of blistering.

There has been fairly rapid erosion of piping in certain isolated locations, generally where such erosion might be expected, and where minimum-thickness holes were present to reveal its progress. These locations were at points of high velocity and turbulence, such as at junctions, bends, or changes in size of pipe. There are, however, unexplained differences between apparently identical configurations that operate under the same conditions in different units. Erosion does not always take place in situations where it might be expected. It is thought that these differences in behavior may be the result of unknown differences in residual stresses in the piping or in vibrational stresses, but this has not been proved.

A corollary of the corrosion problem in the GS process is the deposition of iron sulfide that is formed as a corrosion product. The solubility of iron sulfide in water under GS process conditions decreases with increase in temperature. As the result of this, iron sulfide that is formed by corrosion in cold parts of the system may be precipitated in hot parts. At Dana, and in some of the units at Savannah River where relatively large areas of Type 410 stainless steel are exposed, enough iron sulfide is formed in the process towers to cause serious plugging of the process-waste strippers and their heat exchangers. This precipitation of iron sulfide can be reduced to an acceptable rate by reducing the solubility of iron sulfide at the point where it is formed. This is done by the addition of sulfide ions to the process water in the form of NaHS. This is done routinely at Dana and has been proved effective but not necessary at Savannah River.

CONTROL OF THE GS PROCESS

Operating control of the GS process presents a special problem that is characteristic of any process for isotope separation which depends upon dual-temperature exchange.

In order to set up a driving force and achieve enrichment in a cold tower - hot tower pair, it is necessary to establish and hold within close limits a specific ratio of liquid flow to gas flow. In practice this flow ratio is established by determining the D_2O content of samples taken on a regular schedule from mid-points of the two columns. This procedure frees process control from dependence upon an absolute calibration of flow meters and is essential to successful operation. Process control methods are covered in detail in the Section entitled "Mid-Column Concentrations as Criteria for Control", page 56.

HAZARDS IN HANDLING H_2S

The toxicity of hydrogen sulfide is greater than carbon monoxide and about the same as hydrogen cyanide.

Under operating conditions 600 to 800 tons of H_2S is confined within the GS towers and auxiliaries of such a plant as Dana or Savannah River, and provision for safe handling of this large quantity of toxic gas is an important problem in plant design and operation. All equipment that contains H_2S is located in the open, thus avoiding the hazard of leakage within buildings. Gas monitors that are connected to alarms are placed at strategic points in the general area, and all personnel within the operating area carry gas masks.

The GS units are provided with a system of remotely operated, quick-acting isolation and dump valves. If there is a large leak or rupture, the isolation valves are immediately closed. The possible release is thereby limited to about 8 tons. As soon as the leaking section is

identified, dump valves are opened to discharge the gas in it to a 400-foot flare stack at the top of which the gas is burned. The flare stack is also used routinely for the disposal of small amounts of H_2S that escape from pump and blower seals, are purged from equipment to be repaired, or are discarded to maintain H_2S quality.

DW PROCESS

The DW process, used to concentrate heavy water between 15 and 90%, is a train of continuous water distillation columns that are operated under vacuum.

Feed to the DW process is 15% D_2O from the GS process. An "overhead" fraction containing 3 to 6% D_2O is returned to the GS process.

Towers, reboilers, and condensers for the DW process are fabricated of carbon steel, and there is no significant corrosion problem.

The operating tie-in between the GS process and the DW process is very flexible in that both the quantity and the D_2O content of the product that is withdrawn from the GS process can vary widely without upsetting the DW process.

Operating control of the DW process consists essentially of maintaining a constant flow of steam to the reboilers, and periodically adjusting flows of feed, overhead and product as required to keep the system in balance with the output of the GS plant.

E PROCESS

The basic element of the E process is a bank of electrolytic cells in which water is decomposed to hydrogen and oxygen.

If a mixture of D_2O and H_2O is electrolyzed, the ratio of deuterium to hydrogen in the gas is much less than it is in the liquid from which it was formed so that a separation is possible. The gas mixture is recombined in a burner-condenser, the condensate being depleted in D_2O and the residue in the cells being enriched.

The cells are operated batchwise in a manner that is equivalent to simple distillation. The separation factor for the fractionation, the effective relative volatility of H_2O and D_2O , is between 8 and 10. Control of the E process is particularly simple since the amount that must be electrolyzed to achieve a desired increase in concentration may readily be calculated from the Rayleigh equation for batch distillation. The amount that is electrolyzed is in turn directly related to the number of ampere hours of operation of the cells.

Condensate from the burner-condensers is collected in two or more cuts; the cut of lowest concentration is returned to the DW plant and the others are recharged to the electrolytic cells.

Pure heavy water is obtained from the residue of the E plant cells by evaporation. Before evaporation the residues contain potassium carbonate, which is used and can be reused as electrolyte. This evaporation serves as a final chemical purification of the product, which is then put into aluminum or stainless steel drums for shipment or storage.

H₂S SUPPLY

The H₂S that is required for filling the GS units and replacing losses is made by reaction of sodium hydrosulfide (NaHS) and sulfuric acid. These raw materials are shipped to the plants in tank cars and stored in carbon steel tanks.

The reaction is carried out continuously at atmospheric pressure in a small unit constructed at each location for this purpose. The H₂S gas is compressed and stored as a liquid in carbon steel tanks.

At Dana, the addition of NaHS for the control of iron sulfide deposition is sufficient to provide the necessary make-up gas to the GS units. H₂S is generated in the units by reaction of the sulfide with sulfuric acid that is added to the waste strippers.

WATER SUPPLY

Water at Dana is obtained from gravel beds under the Wabash River by means of Ranney wells. Hardness of about 300 ppm is removed by ion exchange, and the CO₂ that remains after reaction with the ion resin is removed in degassing towers.

Water from the Savannah River is soft, and ion exchange is not required. The treatment at Savannah River consists of filtration, acidification to neutralize alkali carbonate, and degassing to remove CO₂.

PRODUCTION RATES

The Dana and Savannah River Plants were designed to produce heavy water at the same rates, 65 pounds per operating hour or 240 tons per year. These capacities were based on reasonable estimates of attainment in flow rates, operating time, process control, and other factors that influence the output of the plants.

Both plants have in fact exceeded 240 tons per year; Savannah River from the start and Dana during its second and subsequent years of operation. After five years of operation, production at Dana had

risen to about 450 tons per year and at Savannah River to about 500 tons per year.

Four main factors are responsible for the production in excess of the design rates for the GS plants. These are:

1. The gas and water flow rates through the GS towers are considerably higher than the design rates and are near to the absolute maximum at which it is possible to maintain countercurrent flow, i.e., they are run practically at the "loading point". These flow rates are about 1.4 times the original design rating. In order to achieve these flows, antifoam agents are added to the feed water.

2. The temperature spread between the cold towers and the hot towers has been increased beyond the design figure. This requires more steam than was called for in the design; as much steam is used at all times as is available from the power plant.

3. Plate efficiency for the H_2S - HDO isotopic exchange has proved to be greater than was assumed in the design calculations. The design plate efficiency of 40% would permit recovering 16.4% of the D_2O present in the feed water under design conditions of temperature and pressure, (see Table VI). The actual plate efficiency of approximately 60% permits recovery of about 18% of the D_2O , again under design conditions of temperature and pressure.

4. "Time on stream" for the GS units has been increased and approaches 98% at Savannah River and 96% at Dana as compared to the 85% that was used in arriving at the original design rating.

It should be noted that heavy water production at Dana and Savannah River is limited by the output of the GS plants and that the DW and E plants have adequate capacity to handle this output. Extra capacity was provided in the original design of the DW and E plants in order to ensure that these "finishing plants", the small and inexpensive tail end of the process, would under no circumstances be a "bottleneck" that limited the output of the large and expensive front end.

COSTS

In discussing the cost of producing heavy water, it is convenient to consider separately (1) investment, and (2) operating cost excluding capital charges. These two costs can then be combined using the amortization rate that fits the circumstances.

1. Investment The investment in the Savannah River heavy water plant is fairly accurately known since all equipment was installed at the site on one project. Some of the capital equipment at Dana, however, was built in 1940-43 as part of the Wabash River

Ordnance Works, and the actual cost of such items is neither readily available nor applicable. This old equipment includes the steam plant, Ranney wells, pumps, reservoir, and pipe lines from the Wabash River to the site, electric power lines, the DW plant, office building and roads, fences, guard houses, etc.

The total investment in the Savannah River heavy water plant is about \$164,000,000, made up as shown in Table II.

TABLE II

Savannah River Heavy Water Plant Investment

<u>Process Plants</u>	<u>Millions of Dollars</u>
GS Plant	114
DW Plant	2.5
E Plant	1.5
<u>Steam and Electric Power Facilities</u>	31
<u>Water System</u>	8
<u>General Facilities</u> - office building, cafeteria, shops, roads, fences, guard stations, etc.*	7
	<u>164</u>

* This includes mainly the service and general facilities in the heavy water area and does not include any major share of the central administrative and service facilities at the Savannah River Plant.

Some comment on the difference in capital costs between the two heavy water plants is appropriate at this point. Taking \$164,000,000 as the capital investment in the heavy water plant, and dividing this by 470 tons (the annual production), the "investment per annual ton" is about \$348,000, or "per annual pound" about \$174.

The "new money" spent at Dana beginning in 1950 was about \$100,000,000. As previously noted, however, steam, electricity, water, a developed site, and some process equipment were available at the start of the project. The value of these items can only be approximated. A rough estimate, indicates that the cost of building new in 1950 those facilities which were already available for use in the heavy water plant at Dana would have been about \$40,000,000. A representative figure for "investment per annual ton" for Dana would be about \$325,000 or "per annual pound" about \$163.

As previously noted, more of the equipment in the GS plant at Savannah River is made of stainless steel than at Dana and this stainless steel is generally of higher quality (more corrosion resistant). The GS units are arranged in three groups of eight, and two of these groups have towers that are lined with stainless steel. It is estimated that the construction materials of higher quality at Savannah River added about \$10,000,000 to the cost of the GS plant.

Soil-bearing conditions were less favorable at Savannah River for installation of the tall, heavy towers used in the GS units. This is estimated to have added about \$5,000,000 to the cost of the GS plant.

The GS equipment at Savannah River is spread out more than is that at Dana. The Savannah plot plan is favorable as regards control of the H₂S hazard and accessibility for maintenance. The increased spacing between major pieces of equipment, however, added an estimated \$4,000,000 to cost of piping and instrumentation.

Finally, the use of the series cascade in multiple units at Savannah River added to the cost of the GS plant, as previously noted. The added cost for this feature is estimated to be about \$6,000,000.

The direct operating cost for the production of heavy water at the Savannah River Plant is summarized in Table III. The total cost of \$13.41 per pound applies to a production rate of about 490 tons per year, and will vary considerably with production rate. This cost does not include any depreciation or similar capital charges.

TABLE III
Cost of Production of Heavy Water

	<u>Quantity per pound of D₂O</u>	<u>Cost per pound of D₂O</u>
<u>Direct Production Cost</u>		
Feed water, M gal	3.88	\$0.40
Hydrogen sulfide, lb	0.75	.35
Total materials		.75
Salaries		.37
Operating labor		.93
Miscellaneous supplies and expenses		.15
Total direct production cost		<u>2.20</u>
<u>Direct Maintenance Cost</u>		
Labor		1.32
Material		.49
Total direct maintenance cost		<u>1.81</u>
<u>Utilities</u>		
Electrical energy, kwh	320	1.33
Steam (900 psi equiv), M lb	6.4	4.40
Cooling water, M gal.	21	.12
Miscellaneous		.06
Total utilities cost		<u>5.91</u>
<u>Total Direct Cost</u>		9.92
<u>Administrative and General Expense (overhead)*</u>		<u>3.49</u>
<u>Total Expenditures</u>		\$13.41

* The principal single items entering into this cost are:

Analytical control	\$0.36
Technical assistance	.25
Maintenance supervision	.30
Patrol (guards)	.31

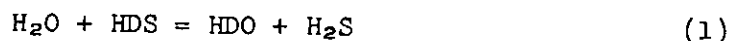
The remaining overhead costs are widely distributed over the usual administrative and service activities.

THE GS PROCESS

FUNDAMENTAL PRINCIPLES

EQUILIBRIUM CONSTANT

The GS process is based on the fact that, in a liquid system involving hydrogen sulfide and water, four compounds exist, H_2O , HDO , H_2S , and HDS^* . These are interrelated by the reaction



the equilibrium constant for which is

$$K_x = \frac{[HDO]_l [H_2S]_l}{[H_2O]_l [HDS]_l} \quad ** \quad (2)$$

This equilibrium constant, and hence the relative proportions of the above components in an equilibrium mixture, varies with temperature. At low temperatures the reaction is displaced further in the direction to $HDO + H_2S$ than it is at high temperatures. This temperature effect is the basis for the use of H_2S as a separating agent for heavy water.

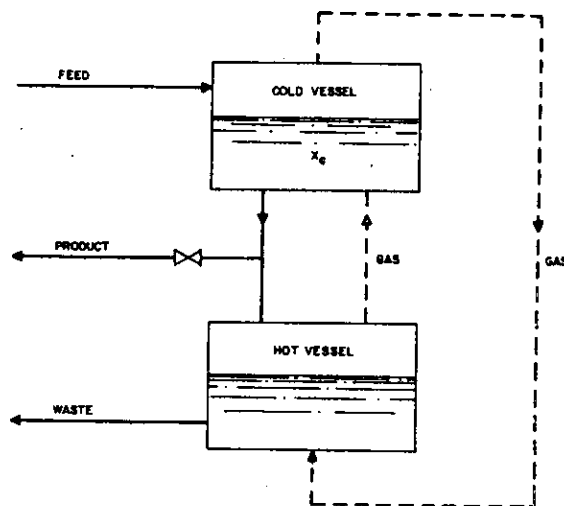


FIGURE 5 - SCHEMATIC ILLUSTRATION OF THE PRINCIPLE OF DUAL-TEMPERATURE SEPARATION

- * At higher concentration D_2O and D_2S enter the picture, but the essential principles are not affected.
- ** Formula shown in brackets with subscript l , e.g., $[HDO]_l$ indicates molar concentration, liquid phase, and the subscript g indicates molar concentration, gas phase, e.g., $[HDS]_g$ in equation (4).

USE OF THE VARIATION OF EQUILIBRIUM CONSTANT TO ACHIEVE SEPARATION

That such a separation is qualitatively possible may be seen by consideration of a system of two vessels through which H_2S gas is circulated in series, countercurrent to a stream of water. The arrangement is shown in Figure 5. In this simplified illustration, gas is bubbled through one pool of liquid in each vessel. Secondary considerations of humidity and solubility are ignored, but it should be noted, however, that H_2S is soluble in water and is free to enter and leave the liquid phase so that HDS can transfer and reach equilibrium between gas and liquid phases. The system will approach a steady state with the pools of liquid in equilibrium with the gas stream at their respective temperatures. Equation (2) can be rewritten,

$$\frac{[HDO]_l}{[H_2O]_l} = K_x \frac{[HDS]_l}{[H_2S]_l} \quad (3)$$

In the idealized case assumed for illustration, and as an approximation in actual operation, the ratio $[HDS]_l/[H_2S]_l$ may be considered to be equal to the ratio in the gas phase. Also, at low concentrations $[H_2O]_l$ and $[H_2S]_l$ are essentially unity so that, again approximately

$$[HDO]_l = K_x [HDS]_g \quad (4)$$

As has been pointed out, K_x varies inversely with temperature, so its value in the cold vessel, K_{xc} is greater than in the hot vessel, K_{xh} . This difference in the value of the constant allows the liquid in the cold vessel to be in equilibrium with the circulating gas at a higher concentration than is that in the hot. Stated algebraically,

$$K_{xc} > K_{xh} \quad (5)$$

hence from equation (4)

$$[HDO]_{lc} > [HDO]_{lh} \quad (6)$$

If nothing is removed from the system at P, at steady state the concentration in the hot vessel must reach the level of the feed concentration, and the concentration in the cold vessel will attain a value that is somewhat higher. Some materials may, however, be withdrawn at P. This will lower the concentration in both vessels somewhat, the hot vessel (i.e., waste) falling below feed concentration and the cold vessel (i.e., product) remaining above. The system thus becomes productive; the feed is split into two streams, one of higher and one of lower than the initial concentration.

APPLICATION OF THE PRINCIPLES TO PRACTICAL OPERATING CONDITIONS

The simplifications that are used for illustration of the principle of the GS process are not permissible in the chemical engineering calculations that are necessary for the design of equipment, and the two-vessel system that is used as the example would produce no worthwhile gain in concentration. In order to achieve practical results, the principle must be applied to the gas-liquid system with proper attention to solubilities and volatilities, and to a continuous countercurrent mass transfer operation so designed that severalfold concentration may be obtained in a single pair of hot and cold vessels.

OVER-ALL DISTRIBUTION CONSTANT

As the foundation for the engineering application of the process, it is necessary to have an accurate relation between the concentration of deuterium in the gas phase and that in the liquid phase. It has been found that these concentrations are related as follows:

$$\frac{x}{y} \frac{(1-y)}{(1-x)} = \beta \quad (7)$$

where x is the mol fraction of D in the liquid phase and y is the mol fraction of D in the gas phase.*

In equation (7) β is a constant whose value is fixed principally by the value of K_x , but which also includes proper allowance for the volatility and solubility of the several components involved. The equation for β in terms of these is

$$\beta = \frac{(1+H)(S+K_x)}{\alpha(1+S)(1+HK_x)} \quad (8)$$

* The designation of concentration of deuterium, the significant isotope in heavy water process systems, requires some explanation. Deuterium may be present either as the only hydrogen isotope or as the half-deuterated molecule e.g., D_2O or HDO (See Appendix A), D_2S or HDS , D_2 or HD , etc. For simplification, the concentration of deuterium, or heavy water, is usually expressed as equivalent D_2 or D_2O . This is the same as the atom percentage of D, $D/(H+D) \times 100$.

The pertinent concentrations in the calculations as they are set up are the over-all concentrations of deuterium in the liquid and gas phases. The concentration in the liquid phase includes D_2O and HDO , liquid, as well as dissolved D_2S and HDS gas. The concentration in the gas phase includes D_2S gas and HDS gas, as well as D_2O and HDO vapor. Mol fractions, again, are in effect the ratio $D/(H+D)$.

In which,

H = mols water vapor per mol of gas in gas phase
 S = mols sulfide gas per mol. of water, dissolved in liquid phase
 α = relative volatility of HDS vs. H_2S , assumed to be equal to relative volatility of HDO vs. H_2O , which value is known and used

$$\alpha = 1.1596 e^{-65.43/T(^{\circ}S)}$$

$$K_x = 1.01 e^{233/T(^{\circ}S)}$$

T = temperature in degrees, Kelvin

A sample calculation of β is given in Appendix B, and graphs of β vs. pressure and temperature are shown in Figures 6A and 6B.

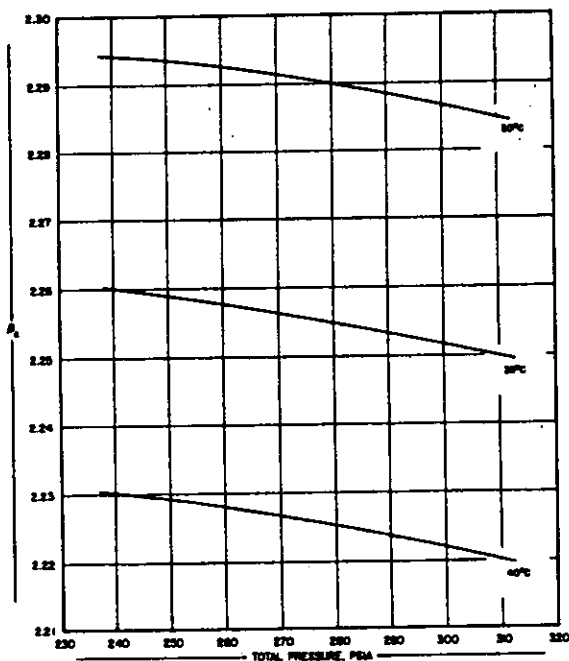


FIGURE 6A - β AS A FUNCTION OF TEMPERATURE AND PRESSURE - COLD TOWER RANGE

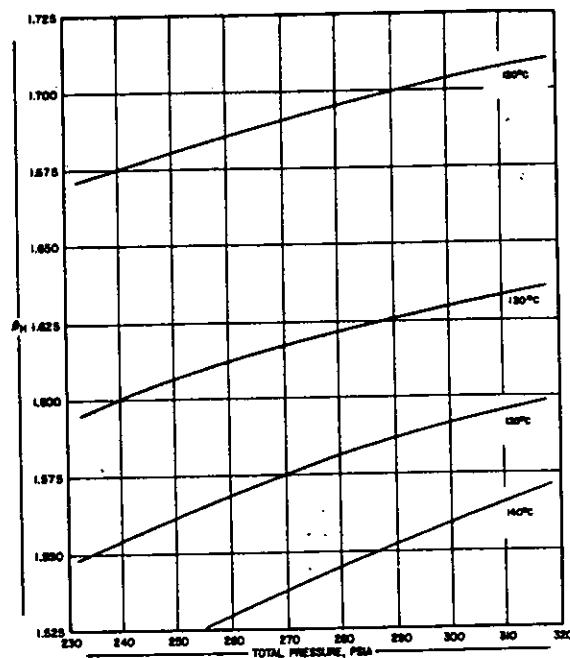


FIGURE 6B - β AS A FUNCTION OF TEMPERATURE AND PRESSURE - HOT TOWER RANGE

In Figure 7 is shown a typical x-y diagram for this system at two temperatures, 30 and 120°C. From equation (7) it is apparent that at low values of x, and therefore of y, the ratio (1-y)/(1-x) is essentially unity so that

$$\beta = \frac{x}{y} \quad (9)$$

This is the equation of a straight line through $x = 0, y = 0$, with a slope equal to $1/\beta$. This straight line relation holds with sufficient precision for this work up to about 1.0% concentration.

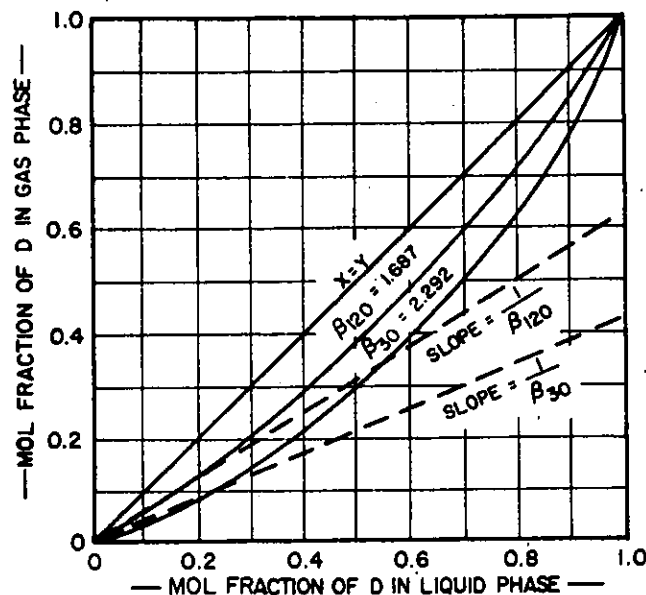


FIGURE 7 - GENERAL GAS-LIQUID EQUILIBRIUM DIAGRAM FOR DANA DESIGN CONDITIONS

CHEMICAL ENGINEERING APPLICATION OF THE PROCESS

EQUIPMENT FOR CONTINUOUS PROCESS

In the discussion of the fundamental basis for the GS process, it has been shown possible, through the medium of gas recirculation, to discharge a waste stream of less than feed concentration from a two-vessel, dual-temperature system, thereby permitting drawoff of product at some higher concentration. In order that the product be produced at significantly higher than feed concentration, it is necessary that the cold and hot vessels be arranged as countercurrent scrubbers. The concentration at bottom of cold and top of hot towers can be built up by feeding natural water to the top of such a cold tower and then in series down through a hot tower whence it leaves as waste, and meanwhile circulating gas upward, first through hot and

then cold towers. A simplified diagram of such a system, including the principal necessary auxiliaries is shown in Figure 8. These auxiliaries are the heat exchange equipment that is required to bring about the temperature changes between hot and cold towers and the stripper which prevents loss of H_2S in the waste stream. All of these units are integrated into a heat recovery system which will be the subject of a separate discussion.

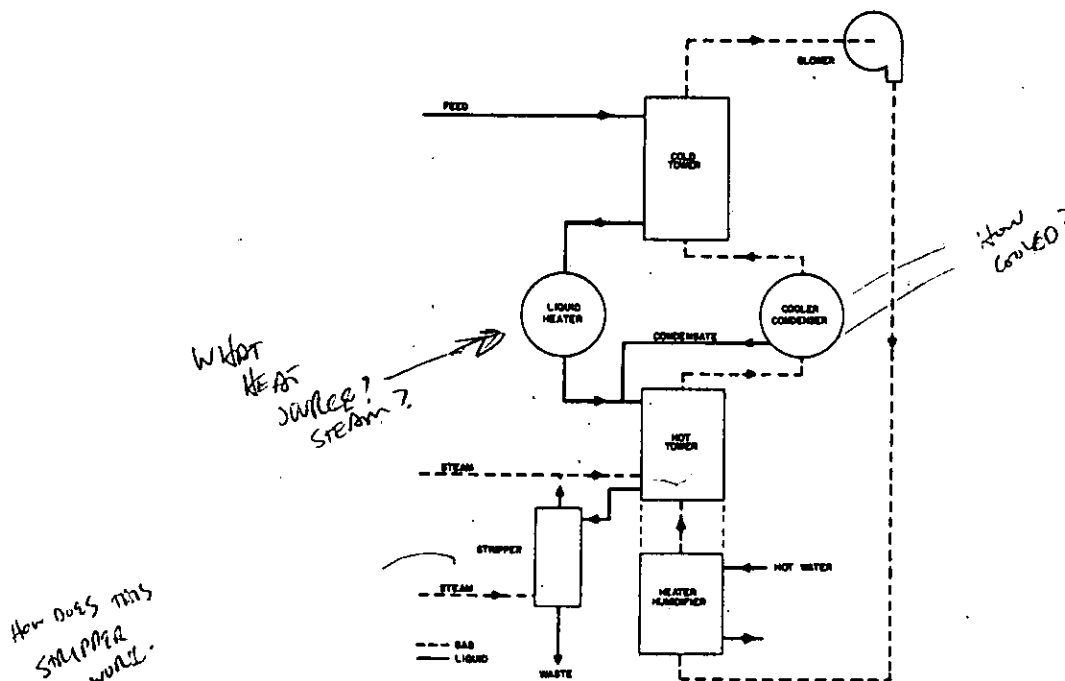


FIGURE 8 - SIMPLIFIED PROCESS DIAGRAM OF A ONE-STAGE GS UNIT

INTERRELATION OF GAS AND LIQUID FLOW RATES

For the present, it is only necessary to note that with the aid of equipment such as is indicated in Figure 8, the system that has been specified can be operated under steady conditions and without loss of the carrier gas, H_2S . It is important to note qualitatively at this time, that the respective liquid and gas flow quantities are not equal in the two towers, and that generally the flow ratios are also different. These differences are due to the internal recycle of water within the hot tower, and to a lesser recycle of gas in the cold tower. Water vapor is added to the cold gas stream as it is heated at the bottom of the hot tower and is subsequently condensed and removed from the hot gas stream that leaves the hot tower. The condensate is added to the liquid stream that enters the hot tower. A similar but much smaller internal recycle of gas occurs in the cold tower because of the solution and dissolution of H_2S in the liquid. Both liquid and gas flows in the hot tower are thus greater than they are in the cold tower, and by roughly the same increments. The effect of this is that the flow ratio in the hot tower has a value between that of the ratio

Subject to the limitations indicated, it is possible to arrange cold tower flows and hot tower flows so that the values of the liquid to gas ratios fall between the values of the slopes of the equilibrium lines. That is, for the low concentrations,

$$\frac{1}{\beta_h} > \left(\frac{L}{G} \right)_h > \left(\frac{L}{G} \right)_c > \frac{1}{\beta_c} \quad (10)$$

FIGURE 9 - GENERAL McCABE-THIELE DIAGRAM FOR A ONE-STAGE GS UNIT

that tends to cause deuterium to migrate from gas to liquid, and in the hot tower from liquid to gas. Since this is so, deuterium can be absorbed in fresh feed water from concentrated gas in the cold tower and the concentrated gas can be produced by stripping D from waste water in the hot tower. As pointed out earlier, the waste can leave the system somewhat depleted in D, and through the mechanism just outlined, a concentrated product can be made available.

TERMINAL GAS AND LIQUID COMPOSITIONS

In connection with Figure 9, page 37, the relative values of the terminal concentrations of gas and liquid streams in the two towers are of interest and are readily explained. To understand the positions of these terminal points on the diagram it is necessary first to recall that at all points in the system the ratio of D to H as the oxide, $\text{HDO}/\text{H}_2\text{O}$, is about twice the ratio of D to H as the sulfide, $\text{HDS}/\text{H}_2\text{S}$.

The significance of this is that the removal of water vapor of relatively high D content by cooling and condensing hot gas results in a lowering of the over-all percentage of D in the gas phase, and similarly, flashing of dissolved gas from cold solution as it is heated results in an over-all increase in percentage of D in the liquid phase.

The feed to the first-stage cold tower is water that contains the natural concentration of D, about 0.0147 mol per cent, and no dissolved H_2S . The first concentration effect as this liquid enters the cold tower is a drop in the value of x from x_f to x_{tc} , brought about by the solution in the water of about 3 mol % of H_2S having a D concentration, y_{tc} , which is about half of natural abundance. Following the gas stream from the top of the cold tower to the bottom of the hot tower, the concentration increases from y_{tc} to y_{bh} , an effect that is brought about by the addition of water vapor to the gas by evaporation of water in the humidifier and by the injection of the steam-gas mixture from the stripper. This water vapor has a concentration, x_{bh} , (assuming that waste water is used for humidification and that all steam goes through the stripper) which is about twice y_{tc} . At the top of the hot tower the gas has some concentration y_{th} , depending upon the flow ratios and number of theoretical plates. As the gas passes through the primary and secondary condensers and into the bottom of the cold tower, water vapor is condensed and returned to the hot tower. This removal of vapor of relatively high D content reduces the concentration in the gas phase from y_{th} to y_{bc} .

The effect of liquid phase concentration between the bottom of the cold tower and the top of the hot tower is of less consequence, but is explainable similarly. Here, the primary effect is the flashing of a relatively small percentage of gas from the liquid, raising the concentration only slightly from x_{bc} to x_{th} .

SELECTION OF OPERATING CONDITIONS

The combination of operating conditions, that is, of temperatures and pressures, for large-scale application of the GS process, was chosen as a reasonable compromise between several somewhat opposing factors. In general, the net separation that is available increases as the temperature spread between hot and cold towers becomes greater. Also, the equipment that is needed is smaller as the pressures at which the process is operated increase. (Because of the quantities of gas to be circulated, the possibility of operating the two towers at appreciably different pressures is quite out of the question economically.)

The temperatures of formation of a liquid phase of H_2S and of a solid H_2S-6H_2O hydrate vary with pressure and fix the lower limits of temperatures for operation of the GS process. These temperatures are tabulated in Table IV.

TABLE IV
Temperatures of Formation
Of Liquid H_2S and H_2S Hydrate

<u>Pressure, psia</u>	<u>Temperature, °C</u>	
	<u>H_2S Hydrate</u>	<u>H_2S Liquid</u>
15	1.1	---
30	7.5	---
50	12.2	---
100	18.6	---
200	25.0	---
300	28.9	---
325	29.5	29.5
400	----	38.6
500	----	48.3
600	----	56.1

As the temperature of the hot tower is increased, the ratio of water vapor to H_2S increases, requiring greater tower cross section. In general, increased temperature spread between the hot and cold tower can be obtained only at the expense of larger heat transfer equipment. In the gas cooler-condensers the effect is most pronounced because of the rapid increase in latent heat load as the water-vapor content of the gas increases with temperature. The latent heat load is also increased as pressure is decreased, for a given set of temperature conditions. As pressures are increased, apart from considerations of hydrate formation and H_2S condensation, the usual problems of leakage, equipment design, and safety are accentuated.

The design conditions for GS plants at Dana and Savannah River are shown in Table VI, page 59. They represent a practical compromise of the many factors of the sort outlined above when applied to the physical location of each plant.

The calculations that are necessary to determine such engineering data as the numbers of plates required in the towers, and the quantity and concentration of heavy water that is produced are carried out by essentially the same fundamental techniques that are used for gas absorption, distillation, and similar diffusional processes. These techniques are based on straightforward material balances over pertinent sections of the process equipment.

RELATIVE GAS AND LIQUID FLOW RATES

One of the most useful sections over which to make such material balances is outlined "AA" in Figure 10, from which a number of pertinent equations can be derived. From an over-all balance of total flows,*

$$L_c + G_h = L_h + G_c + L_p \quad (11)$$

An H_2S balance without regard to isotopic content results in

$$L_c \frac{(S_o)}{(1 + S_c)} + G_h \frac{(1)}{(1 + H_h)} = L_h \frac{(S_h)}{(1 + S_h)} + G_c \frac{(1)}{(1 + H_c)} + 0 \quad (12)$$

assuming that product, L_p is stripped of H_2S .

A similar water balance gives

$$L_c \frac{(1)}{(1 + S_c)} + G_h \frac{(H_h)}{(1 + H_h)} = L_h \frac{(1)}{(1 + S_h)} + G_c \frac{(H_c)}{(1 + H_c)} + L_p \quad (13)$$

and, on the basis of total deuterium, irrespective of molecular species,

$$x_c L_c + y_h G_h = x_h L_h + y_c G_c + x_p L_p \quad (14)$$

Under steady operating conditions, each of these equations must be satisfied. Equations (11), (12), and (13) correlate the over-all flows of the carrier streams irrespective of deuterium content. Since in these equations, S and H , the mol ratio solubilities and humidities, are constants that have been fixed by the conditions of operation, and P , the product rate is generally fixed, the equations may be solved to determine hot tower flows as related to cold tower flows. It should be noted, however, that there are actually but two different equations relating four flows so that the absolute flow rates are not fixed. Any two flows or one flow ratio may be set, and the other flow calculated relative to them. Calculations that involve the concentration and production rate of D_2O are based on equation (14) after the relative values of L and G have been determined.

* For definition and explanation of symbols see Appendix C.



Material balances analogous to equation (14) may also be made over the lower section of the cold tower ("BB" in Figure 10) and over the upper section of the hot tower ("CC" in Figure 10). For the cold tower,

in which x_c and y_c are the corresponding liquid and gas phase compositions for any plate in the tower. From this,

This is the equation relating y_c , the concentration of D in the gas from any plate, to x_c , the concentration in the liquid on that plate, or the "operating line" of the McCabe-Thiele-type diagram for calculating concentrations through the tower. Since x_{bc} and y_{bc} are the fixed terminal values for the tower and L_c and G_c are constant flow rates, the equation is that of a straight line of slope L_c/G_c , and y-intercept

- 41 -

The analogous equations for the hot tower are, by material balance over "CC",

$$G_h y_h + L_h x_{th} = G_h y_{th} + L_h x_h \quad (17)$$

and

$$y_h = \frac{L_h x_h}{G_h} + y_{th} - \frac{L_h x_{th}}{G_h} \quad (18)$$

RECOVERY OF D₂O FROM FEED - SIGNIFICANCE OF THE X-INTERCEPT OF OPERATING LINE

Equation (14) may be rearranged as follows:

$$(L_c x_c - G_c y_c) - (L_h x_h - G_h y_h) = x_p L_p \quad (19)$$

In this equation, $x_p L_p$ is the quantity of product material withdrawn times its D₂O content, in other words, the net recovery or production of D₂O for the system. The term $(L_c x_c - G_c y_c)$ represents the net transport of D₂O down the cold tower, toward the point of product withdrawal; the term $(L_h x_h - G_h y_h)$ represents the net transport down the hot tower, away from the point of product withdrawal. For the generalized values of x and y in equation (19), the terminal values for the bottom of the cold and top of the hot towers may be substituted [see equations (15) and (17)], giving:

$$(L_c x_{bc} - G_c y_{bc}) - (L_h x_{th} - G_h y_{th}) = x_p L_p \quad (20)$$

Returning now to equation (16), the equation of the operating line, by setting $y_c = 0$ and letting the corresponding value of $x = x_{c_o}$, the following relation is obtained,

$$\frac{(L_c)}{(G_c)} x_{c_o} + y_{bc} - \frac{(L_c)}{(G_c)} x_{bc} = 0 \quad (21)$$

Whence,

$$L_c x_{c_o} + G_c y_{bc} - L_c x_{bc} = 0 \quad (22)$$

and

$$L_c x_{c_o} = (L_c x_{bc} - G_c y_{bc}) \quad (23)$$

Similarly, for the hot tower, if $y_h = 0$ and the corresponding value of x is x_{h_o} , from equation (18) is obtained

$$L_h x_{h_o} = (L_h x_{th} - G_h y_{th}) \quad (24)$$

Substituting (23) and (24) in equation (20)

$$L_c x_{c_o} - L_h x_{h_o} = x_p L_p \quad (25)$$

This equation is of interest since it relates the recovery or production rate to liquid flows only, and since the terms x_{c_0} and x_{h_0} are, respectively, the x-intercepts of the cold and hot tower operating lines on the gas-liquid concentration diagram for the system. The relative positions of these intercepts for normal operation of a first-stage tower pair is indicated in Figure 11.

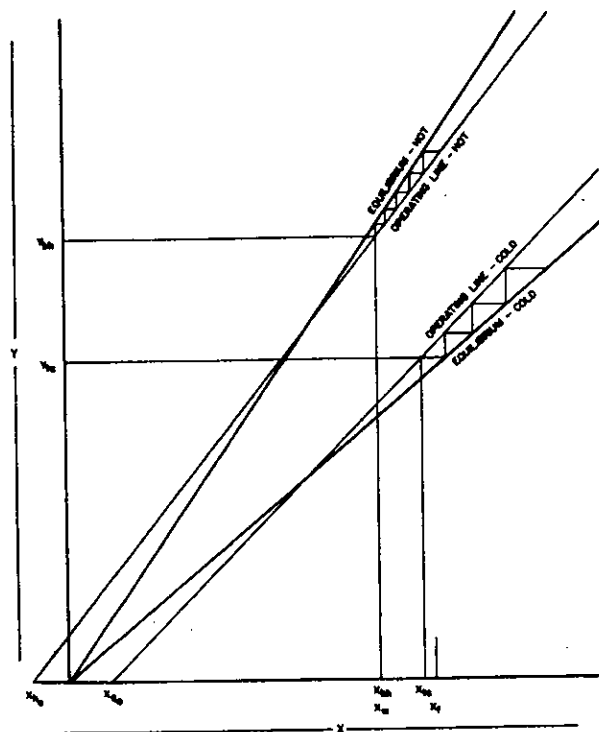


FIGURE 11 - DIAGRAM ILLUSTRATING X-INTERCEPTS OF OPERATING LINES

It will be noted that for normal operation x_{h_0} is negative and x_{c_0} is positive. The effect on these intercepts of deviations from normal operation will be discussed later. The values of these terms have no physical significance but are valuable for use in calculations involving the GS process.

EFFECT OF CHANGES IN RATE OF PRODUCT WITHDRAWAL

It is informative to comment at this point on the effect of rate of product withdrawal on the operation of a GS process unit, whether of one or of several stages. It should be noted that operating temperatures and pressures of the unit are restricted to fairly narrow ranges by design, that the flow rate of gas through the system is logically held at maximum permitted by tower size, and that flow of liquid must be held in proper ratio to flow of gas. The determination of these rates will be discussed later. If these flow rates are maintained, however, for that matter at any steady condition of

operation, the concentration of product that is withdrawn from the unit will be a function of the rate at which it is withdrawn, the highest concentration being attained as the rate approaches zero.

The reason for the interdependence of rate of withdrawal and quality of product can be seen with the aid of Figure 12. On this figure, essentially similar to Figure 11, are shown two additional sets of operating lines. One pair of these lines, Figure 12a, passes through $x = 0, y = 0$, so that from equation (25) it is apparent that the production of D_2O must be zero. Comparison of the length of the steps (each achieved by one theoretical plate) on the concentration diagram with those for normal conditions (Figure 12b), shows however, that the concentration that is achieved in the number of plates available will be very much greater for operation with no net production ("locked in") than for normal operation. In Figure 12c the case is shown for maximum recovery and (with any finite number of plates) negligible concentration gain. In this case, the operating lines are displaced laterally, away from the origin, and are made to intercept the equilibrium lines at the feed and waste concentrations. A stepwise increase of concentration cannot be indicated for this case, and in fact, the condition is significant only as a limiting condition.

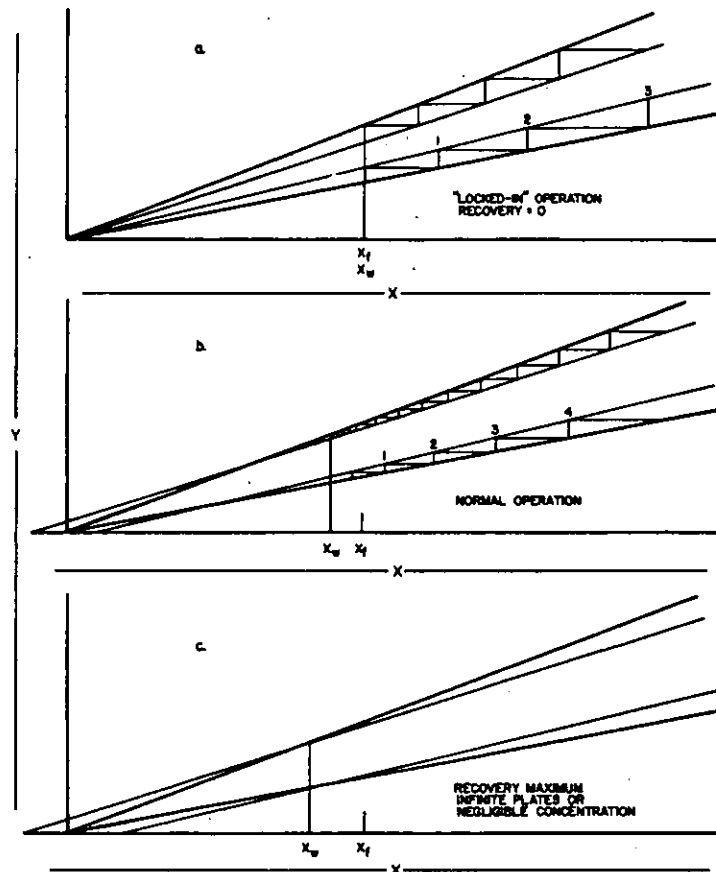


FIGURE 12 - EFFECT OF RATE OF RECOVERY ON CONCENTRATION GAIN

STAGING

The concept of the x-intercept as it is related to recovery and unit flows leads logically into a discussion of the matter of staging. In Figure 11 it can be seen that since the operating lines diverge from the equilibrium lines as concentration increases, the concentration gain per theoretical plate increases, the increase being exponential. The gain per plate also depends on the location of the operating line laterally relative to the equilibrium line, that is to say, upon the x-intercept. For a given net recovery of product, then, a pair of GS towers can be designed for relatively small gain per plate, necessitating a large number of plates but relatively low liquid and gas rates and hence low tower cross section [see equation (25)], or at the expense of tower area, the number of plates can be reduced. With natural water feed at only 0.0147 mol % D_2O , the x-intercepts for the GS unit operating lines must be very near to zero in order to achieve any concentration. This means that for significant production, high flow rates and large equipment are needed. As the concentration increases through the towers, however, the possibility arises of shifting the operating lines to increase the spread between the x-intercepts, and thus to permit the product to be carried at lower flow rates but with smaller gain per plate and hence at the expense of more plates. This possibility is illustrated in Figure 13.

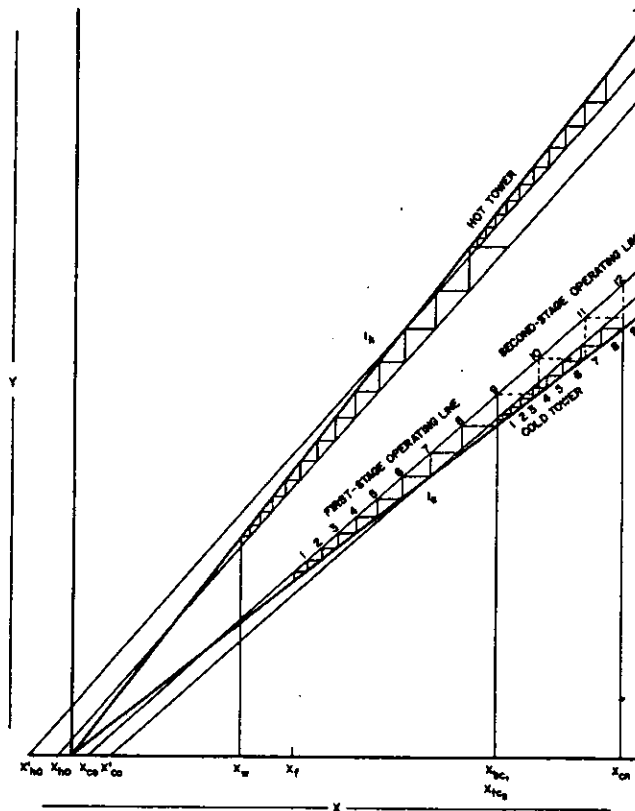


FIGURE 13 - ILLUSTRATION OF THE EFFECTS OF STAGING

In this figure, the first-stage cold and hot tower operating lines have intercepts x_{c0} and x_{h0} , respectively so chosen that the gain per plate at the low-concentration end of the diagram will be reasonable, though small. Within about 10 plates, however, the gain per plate reaches about fourfold the initial value. At this point it is possible to spread the operating lines (they remain parallel to their former positions) so that they intercept at x'_{c0} and x'_{h0} . This permits reduction of absolute flows in the hot and cold towers by the ratios x_{h0}/x'_{h0} and x_{c0}/x'_{c0} , respectively, (reduction in tower cross section) but results in reversion to small steps on the concentration diagram. Note that if the large steps of Stage 1 had been continued, instead of staging after 9 theoretical plates, the concentration x_{cn} would have been attained in 12 plates instead of 18. Staging is economical because the reduction of flow rates, and hence diameter of towers, holdup of product, and size of auxiliary equipment, outweighs the cost of additional plates and tower height.

INTERSTAGE TRANSFER

The stages of a GS unit could be interconnected in a number of ways. The arrangement which is being used is, however, probably the simplest so far as equipment is concerned. A simplified flow diagram for the system that is used at Dana is shown in Figure 14. A portion (at Dana 25%) of the liquid leaving the cold tower of the first stage (CT-1), instead of going to the liquid heater and thence to the hot tower (HT-1), is pumped directly to the top of the second-stage cold tower, (CT-2). The liquid passes downward through CT-2 and through the second-stage liquid heater except that, again, 25% of the cold liquid is pumped to the top of the third-stage cold tower. In the three-stage unit that is illustrated, this last liquid stream passes in series through the third-stage cold tower, the third-stage liquid heater and the third-stage hot tower. From the hot tower it returns to the second stage, joining liquid from the second-stage liquid heater to enter the second-stage hot tower. The liquid from the second-stage hot tower joins liquid from the first-stage liquid heater, passes through the first-stage hot tower and goes to the waste stripper. The gas stream follows an exactly analogous course countercurrent to the liquid, with the exception that gas leaving the first-stage cold tower is recycled to the bottom of the corresponding hot tower. In Figure 15 this arrangement is shown in a different and quite schematic manner. The towers of the three stages are represented as vertically superimposed blocks of progressively diminishing width. This diagram points out more clearly than does Figure 14, that the units are in effect "conical" towers, diminishing in size as concentration increases, and that until the last stage of the train is reached there is no stream that can properly be thought of as a "drawoff" of enriched material. The stage-to-stage flows of gas and liquid are no different in function from the plate-to-plate flows within a tower.

PV

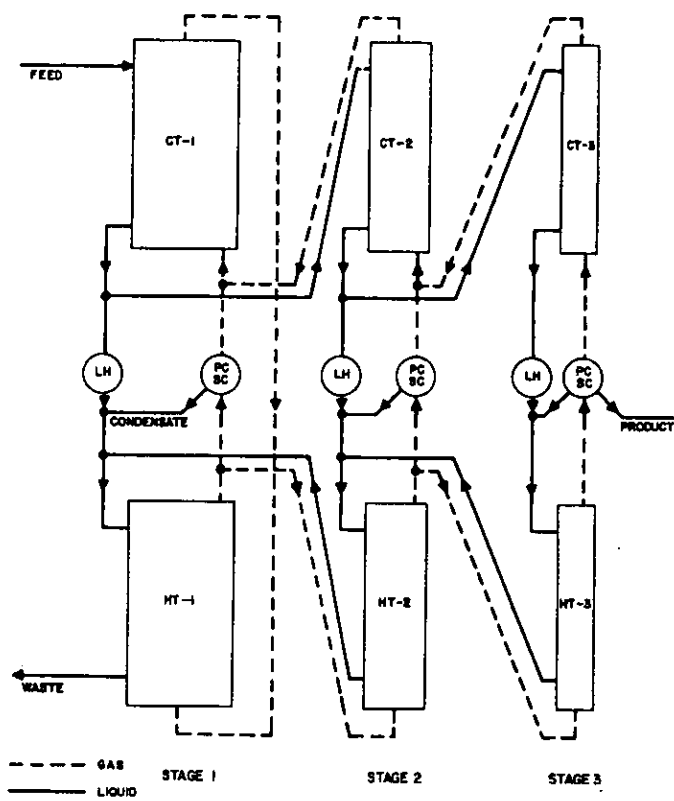


FIGURE 14 - SIMPLIFIED PROCESS FLOW DIAGRAM OF A THREE-STAGE GS UNIT

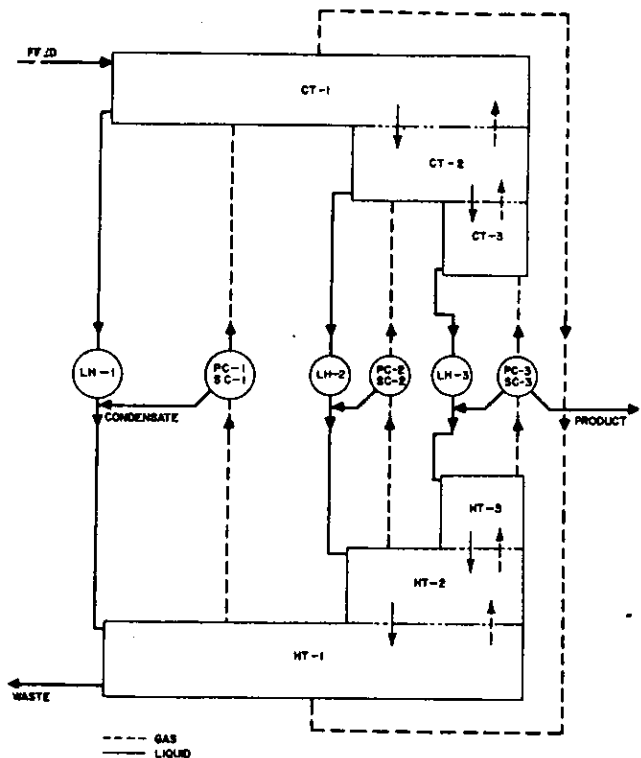


FIGURE 15 - SCHEMATIC DIAGRAM OF A THREE-STAGE GS UNIT

The system that is used at Savannah River is similar but involves only two stages. The second stage is composed of two towers and two hot towers in series. A simplified flow diagram is the same as Figure 14, but without a Stage 3. The product is withdrawn from the Stage 2 PC and SC condensate. On a design basis, about 29% of the liquid leaving the cold tower of the first stage is pumped to the top of the second-stage cold tower. Also, about 29% of the gas leaving the top of the first-stage hot tower is directed to the base of the second-stage hot tower.

Before leaving the subject of interstage flows it is of interest to note the relative liquid and gas compositions with respect to D in the four streams joining two stages. Figure 16 is an x-y diagram which illustrates the situation. Points "a" and "b" represent the coexisting compositions at the bottom of the first-stage cold tower and top of the first-stage hot tower, respectively. Points "c" and "d" are the respective values for the second-stage cold and hot towers. Since the liquid at the top of the second-stage cold tower has come directly from the bottom of the first-stage cold tower, $x_{tc2} = x_{bc1}$. Similarly, $y_{bh2} = y_{th1}$. One of the coordinates of both "c" and "d" are thus fixed and the other is determined by the flow rates chosen for the higher stage in accordance with the flow rate - recovery relationships that were previously discussed. The values of x_{th1} and y_{bc1} are the values that would be obtained if there were no higher stage connected. Actually, both would be slightly lower because of the return of more dilute material from Stage 2.

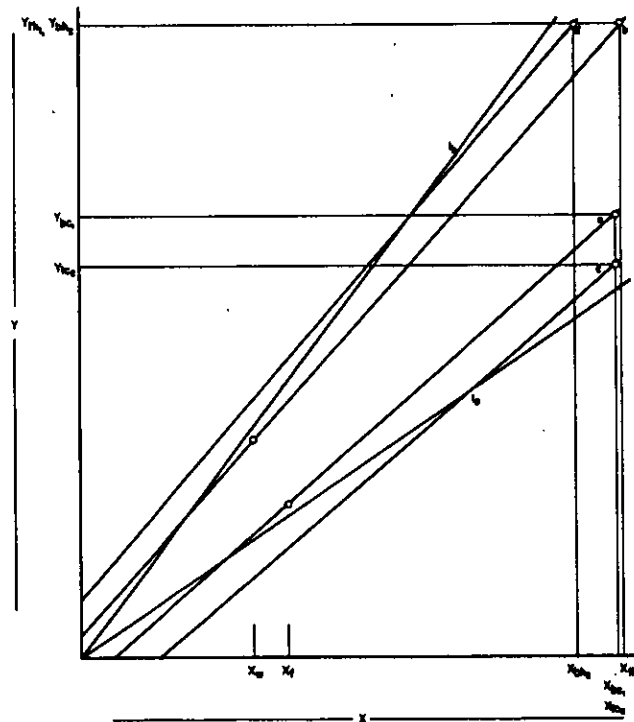


FIGURE 16 - DIAGRAM ILLUSTRATING INTERSTAGE CONCENTRATIONS

In connection with the consideration of interstage transfer it is important to note that the design rate of transfer of product from one stage to another can take place only if the design concentration of product is maintained. Referring to Figures 13 and 16, for given recovery and flow rates, the slopes and x-intercepts of the second-stage operating lines are fixed. The operating lines intercept the equilibrium lines at I_c and I_h , and these points represent the minimum concentrations at which the net production can be transferred into the second stage, regardless of the amount of further concentration that may take place there. Actually, I_c and I_h are limiting values that would result in negligible increase in concentration over any real number of plates in Stage 2. For the design concentration increase to be achieved in the second stage, with fourfold reduction in flows, the first stage must first have achieved its fourfold concentration of feed water.

CALCULATION OF CONCENTRATION AND NUMBER OF THEORETICAL PLATES

The concentration that will be attained in a given number of plates, or the number of plates that are required to achieve a given concentration in a GS unit may be calculated by procedures equivalent to the McCabe-Thiele method that is commonly applied to distillation problems. In order to use these procedures the equations of the operating line, that is, the slope, (L/G) , and the intercept (or some other point on the line) must be fixed. Assuming that the number of theoretical plates in the hot tower of a unit is to equal the number in the cold tower, optimum results will be obtained from the system when the following two conditions are met, first, that the ratio of the slope of the hot equilibrium line to the slope of the hot operating line equals the ratio of the slope of the cold operating line to the slope of the cold equilibrium line, and second, that a similar equality exists between the ratios of actual and equilibrium gas compositions at the top of the cold tower and the bottom of the hot tower. The first of these conditions may be expressed as

$$m_h/R_h = R_c/m_c \quad (26)$$

where m = slope of equilibrium line, $1/\beta$
 R = slope of operating line, L/G

From which,

$$\frac{L_c}{G_c} / \frac{1}{\beta_c} = \frac{1}{\beta_h} / \frac{L_h}{G_h} \quad (27)$$

The second conditions may be expressed,

$$\frac{x_{tc}}{\beta_c y_{tc}} = \frac{\beta_h y_{bh}}{x_{bh}} = u \quad (28)$$

Where u is the degree of approach to equilibrium* in the tower.

*. If the value of u is 1.0, the operating and equilibrium lines intersect at x_{tc} and x_{bh} and an infinite number of plates would be required.

Equation (27) provides a third relation between tower flow rates that can be used with equations (12) and (13) and solved for the optimum ratios. The value of u defines the intercepts of the operating lines and hence the recovery of D_2O achieved.

Under the conditions of temperature and pressure that were selected for the Dana GS process, the upper limit of recovery is 20% of the D_2O content of the feed water. To attain this percentage recovery would require an infinite number of theoretical plates, but the flows and hence the cross-sectional area of the towers would be at minimums. The design recovery of 16% represents a practical compromise between these opposing factors. For a recovery of 16% the value of u is 0.98. The selection of a numerical value for u is the starting point for the equipment design of a GS unit which will produce a given number of mols of heavy water with a given concentration gain in each stage.

The factors determining the relative values of the terminal concentrations, x_{tc} , y_{tc} , x_{bh} , and y_{bh} have been pointed out qualitatively on page 38. Quantitatively, for the conditions chosen, the relationships are as follows:

$$y_{tc} = \frac{x_{tc}}{0.98 \beta_c} \quad (29)$$

$$y_{bh} = \frac{0.98 x_{bh}}{\beta_h} \quad (30)$$

The value of y_{bh} is tied to that of y_{tc} and x_{bh} by considerations of material balance. The total gas flow, G_h in the bottom of the hot tower which has the composition y_{bh} , is made up of G_o , the gas from the top of the cold tower, the H_2S stripped from L_h in the waste stripper, which can be designated as G_s , and the remainder, G_w , water vapor supplied by evaporation in the humidifier and with the gas from the stripper. The quantities are related as follows:

$$G_h = G_o + G_s + G_w \quad (31)$$

$$G_s = L_h \frac{(S_h)}{(1 + S_h)} \quad (32)$$

$$G_o = G_c + L_o - L_c \quad (33)$$

$$L_c = L_o (1 + S_c) \quad (34)$$

The corresponding compositions are

$$G_h \text{ --- } y_{bh}$$

$$G_s \text{ --- } y_s \quad y = \frac{x_{bh}}{K_{xh}}$$

$$G_o \text{ --- } y_{tc}$$

$$G_w \text{ --- } x_{bh}$$

An equation can thus be written that relates these concentrations and quantities as follows:

$$G_h y_{bh} = G_o y_{tc} + G_s \frac{(x_{bh})}{(K_{xh})} + G_w x_{bh} \quad (35)$$

This is simply a deuterium balance around the bottom of the hot tower.

Within the limits of precision of the data, and within the operating limits of the process flows, x_{tc} can be taken as 1.45×10^{-4} (mol fraction) if x_f is 1.47×10^{-4} . The difference, 2×10^{-6} , is small and relatively constant since it results from dissolving in 100 mols of feed water about 3 mols of H_2S which varies in composition from 6×10^{-5} to 7×10^{-5} over the range of operations encountered.

With the concentration at the top of the cold tower and bottom of the hot tower of the first stage defined, and the liquid and gas rates and hence the slopes of the operating lines known, it is now possible either to determine the number of theoretical plates that are required to attain any assumed concentration, or to calculate the concentration that will be reached with a given number of plates. This may be done graphically by drawing in the individual steps between accurately drawn operating and equilibrium lines or, since in the dilute region which is of most concern, both operating and equilibrium lines are straight, the problem may be solved algebraically. For this solution the Colburn method ⁽⁶⁾ or its equivalent may be used. The Colburn equation is:

$$N_p = \frac{\log [(1-P) M + P]}{\log 1/P} \quad (36)$$

In the reference article as well as in Perry ⁽⁷⁾, charts are presented for simplified solution of this equation. In the equation, P is the appropriate ratio of slopes of operating and equilibrium lines. In the cold tower,

$$P_c = \frac{m_c}{R_c} \quad (37)$$

and in the hot tower

$$P_h = \frac{R_h}{m_h} \quad (38)$$

The term M is the enrichment ratio for the tower. In the cold tower

$$M_c = \frac{y_{bc} - m_c x_{tc}}{y_{tc} - m_c x_{tc}} \quad (39)$$

in the hot tower

$$M_h = \frac{\frac{x_{th} - y_{bh}}{m_h}}{x_{bh} - \frac{y_{bh}}{m_h}} \quad (40)$$

Since the slopes of all lines are known, x_{bc} can be calculated from y_{bc} and x_{tc} , and y_{th} can be calculated from x_{th} and y_{bh} .

This equation is equivalent to a more general form which has also been used,

$$A = a \frac{(Q^n - 1)}{(Q - 1)} \quad (41)$$

in which a is the enrichment obtained in the first theoretical plate, A is the enrichment over n plates, and Q is the reciprocal of P .

The relationships of the various terms used in the above equations are illustrated in Figure 17. A sample calculation of optimum liquid and gas flows and terminal concentrations for a Dana first-stage unit is presented in Appendix B.

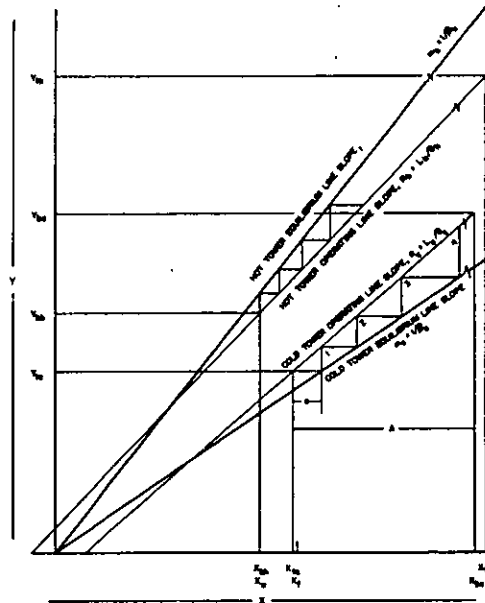


FIGURE 17 - McCABE-THIELE DIAGRAM ILLUSTRATING METHOD FOR CALCULATING CONCENTRATION GAIN AND NUMBER OF PLATES

PLATE EFFICIENCY

All of the calculations of concentration attained in the GS units are based on theoretical plates. The actual plates in a tower are not, however, 100% efficient, that is, they do not succeed in bringing the gas and liquid compositions to the values that correspond to successive steps on the McCabe-Thiele diagram for the tower. The plate efficiencies for the GS process, i.e., the ratio of the number of theoretical plates that are required for a given concentration gain to the number of actual plates, expressed as a percentage, were originally estimated to be 43% in the cold tower and 50% in the hot tower. The design production and yield of the units were based on these figures. As has been pointed out, the plate efficiencies are actually about 60% in the cold towers and 65% in the hot towers. These higher efficiencies have increased the degree of approach to equilibrium (u) to about 99%.

EFFECTS OF DEVIATIONS FROM OPTIMUM FLOW RATIOS

In order to get some idea of the precision of control that must be maintained for satisfactory operation of the GS process it is necessary to investigate the manner in which deviations from design conditions may affect the operation, and to evaluate the magnitude of such effects. It has already been stated that there are optimum flow ratios for the system, and that assuming an equal number of theoretical plates in the hot and cold towers of a unit, the flows should be such that the ratios of slopes of the operating and equilibrium lines in the two towers are equal. The number of theoretical plates in a GS unit is fixed, neglecting the effects of slight variations in efficiency that may be caused by changes in flow rates. Since this is so, the number of steps on the McCabe-Thiele diagram for a tower operating between any terminal concentrations is also fixed. The flow rates in the system are variable, that is to say, controllable, subject to the physical considerations that interrelate those flows. The significance of this is that if the concentration of D_2O at the base of the cold tower of a GS unit is maintained at a prescribed value through adjustment of rate of product withdrawal from the system, and the liquid-to-gas ratios are varied, the concentration gradients within the towers will adjust so as to shift the operating lines laterally and thus to maintain the number of steps between top and bottom concentrations equal to the number of available theoretical plates. The manner in which such shifts may occur is illustrated in Figures 18a, b, and c. In these three diagrams, cases for optimum, low, and high liquid-gas ratios are shown. The diagrams are drawn in approximately the right proportions to correspond with Dana GS first-stage operation, but show only nine theoretical plates in each tower so that the scale can be sufficiently large to illustrate the points to be made.

Figure 18a is the diagram for normal operation in which the conditions of equations (26) and (28) are met. In this diagram which is to serve as a datum for comparison, the distance r , and the spread between x_f and x_w are roughly proportional to the recovery (production) of D_2O in the unit. Figure 18b is so drawn that with liquid - gas ratios reduced below the optimum values until the cold tower operating line is parallel to the equilibrium line, and with the slope of the hot tower line reduced correspondingly, there are still nine theoretical plates indicated in each tower to reach the terminal concentration x_b . It is apparent that under these conditions the recovery as indicated by r' and the difference between feed and waste composition, x_f and x_w' are less than in Figure 18a. In Figure 18c the opposite case from Figure 18b is shown, that in which the ratios are higher than optimum, with the hot tower operating line parallel with its equilibrium line. It is apparent that the effect of deviation from optimum ratios in this direction is much the same as in the previous case. Careful comparison of the three diagrams will disclose the manner in which the concentration steps differ. In general, as the divergence of operating and equilibrium lines increase, the spread between the lines at the low-concentration end decreases.

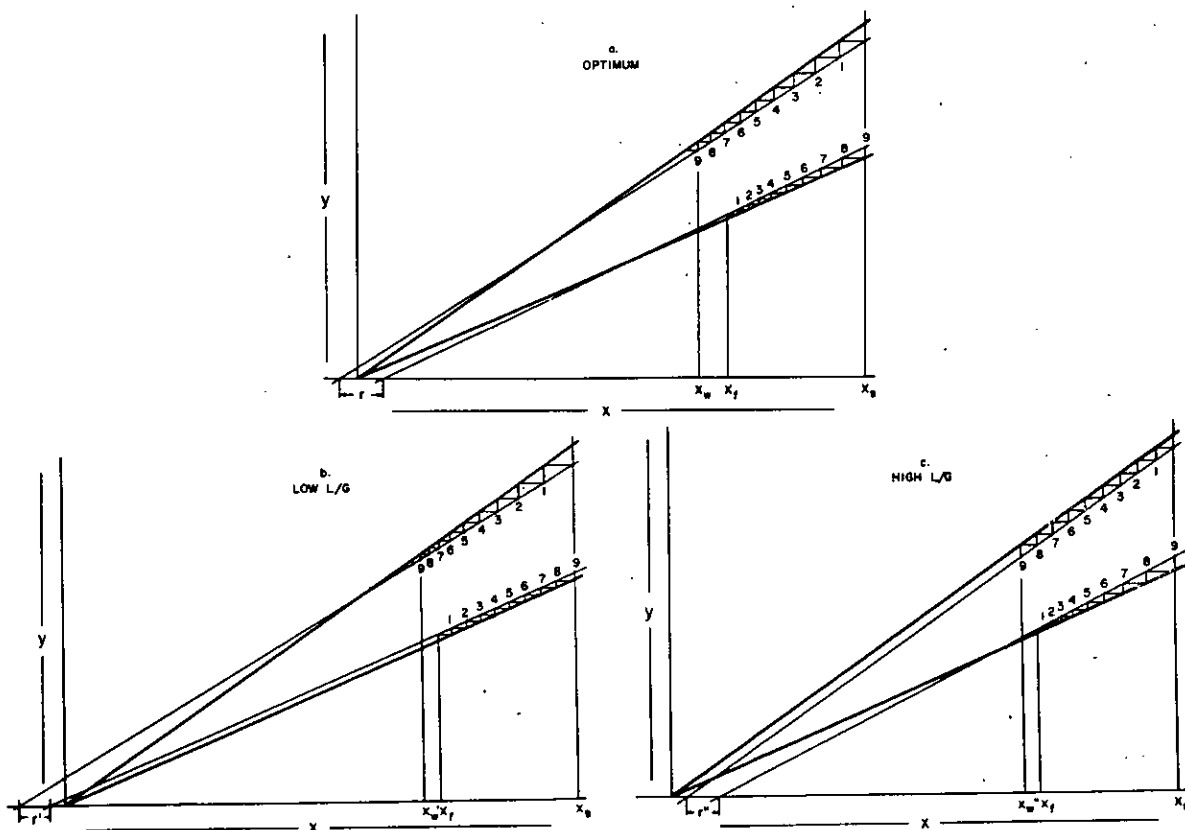


FIGURE 18 - McCabe-Thiele Diagram Illustrating Effects of Deviation from Optimum Flow Ratios

The illustrated cases do not represent limits of the deviation of flow ratios. Progressively greater deviation in either the high or low direction will further reduce the spread, r , and hence the recovery, until for the given concentration x_g , $r = 0$ and $x_w = x_f$, and the net recovery then becomes zero. In these cases the operating lines will actually converge on the equilibrium lines in the hot and cold towers for the high- and low-ratio cases, respectively.

Quantitatively the effect of variation in liquid-gas ratio for a Dana GS unit is shown in Figure 19 and Table V. As is pointed out in the table, the analysis was based for design purposes on the gas rate through the hot tower as the fixed limiting factor on throughput. The feed rate to the system corresponding to this gas rate increases as the liquid-gas ratios increase. The assumed concentration is the design value for the base of the first-stage cold tower, approximately fourfold increase over feed concentration.

The data shown for current plant operation (Table V) have been computed using current plant operating conditions and the experimentally determined plate efficiencies.

The data that are presented in Table V and Figure 19 are based on the assumption that the first-stage base concentration remains at 0.06%, and therefore indicate the loss in productivity that is caused by a short-term upset of the liquid-gas ratio. If the upset is of long duration, concentration levels drop all along the cascade, and at a lower first-stage base concentration some of the lost productivity tends to be restored. The essential consideration, however, is that high production is attainable only by holding the flow ratio at or close to the optimum value.

TABLE V

Effect of Variation of Liquid-to-Gas Ratio on Water
Feed Rate and Net Recovery of Product - Dana Unit

Basis: Design - $G_h = 74,000$ mol/hr in 4 HT's
Current average operating conditions, 30°CT, 135°HT

$R_c = L_c/G_c$	Feed Rate L_o , mol/hr	Recovery, mol D_2O /hr
0.436	27,500	0
0.460	29,100	0.875
0.481	30,400	0.945
0.488*	30,800	0.970
0.543	34,400	0.630
0.553	34,900	0

* Optimum

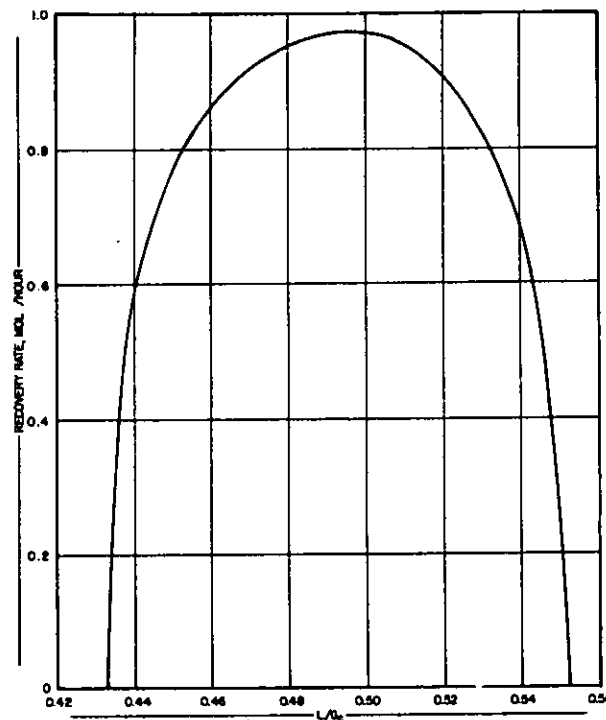


FIGURE 19 - RECOVERY RATE vs. $(L/G)_C$ - DANA CONDITIONS

MID-COLUMN CONCENTRATIONS AS CRITERIA FOR CONTROL

It was found early in the operation of the Dana pilot plant that analyses of samples taken from the mid-points of the hot and cold towers provided the most useful and sensitive criteria for control of flows in the unit. Comparison of these analyses gave an indication as to the direction and approximate magnitude of deviation from the optimum ratios.

In the pilot plant, operating "locked-in", that is without drawoff of concentrated material, the maximum concentration gain was achieved when the concentrations at the mid-points of the cold and hot towers were equal. That this should be so is apparent if three points are recalled. First, for "locked-in" operation, when the system has built up to steady concentrations, the waste from the hot tower has the same concentration as the feed to the cold tower. Second, for the maximum concentration to be attained, the values of P_c and P_h , the ratios of the slopes of the operating and equilibrium lines in the towers should be equal. Third, with zero recovery under the conditions postulated, two operating lines will pass through the origin on the x-y diagram. Under these conditions the given number of theoretical plates will achieve the same concentration in either tower, and any inequality will be evidence of deviation from the second of the three conditions, that is of deviation from optimum liquid-gas ratios. The plates at the mid-points of the columns are most sensitive to these deviations since,

no matter what flow ratios are held, the concentrations at the top of the cold and bottom of the hot towers and at the bottom of the cold and the top of the hot towers must respectively be about equal.

In the producing plants the same relationship holds true up to concentrations of 3 mol per cent D_2O , i.e., the L/G is optimum when the ratio of cold and hot tower mid-column sample concentrations is equal to 1.0. At concentrations above 3 mol per cent the mid-column ratio for optimum production increases slowly reaching a value of 1.5 at 15 mol per cent D_2O . This change is the result of curvature of the equilibrium line at the higher concentrations. The curvature causes a pinching out of the cold tower operating line at the rich end and the hot tower operating line at the lean end more rapidly than predicted by theory based upon straight equilibrium lines. The operating lines must therefore be shifted at the higher concentrations to distribute this pinching effect equally between the hot and cold towers, resulting in an increase in the optimum mid-column concentration ratio. These effects appear in the operation of the fourth and fifth stage of a Dana unit and in the rich end of the second stage of a Savannah River unit.

Once the concentration effect is taken into account the mid-column ratio at optimum L/G is dependent only upon the plate efficiencies of the cold and hot towers, and therefore provides an excellent means of control which is not dependent upon other process conditions.

Deviation from optimum flow ratios in either direction, as has already been pointed out, causes a decrease in concentration or recovery - one of these being held constant. If the deviation is in the direction of low liquid - gas ratios, the concentration of D_2O at the mid-point of the cold tower will be higher than the concentration at the mid-point of the hot tower. If the liquid-gas ratios are high, the concentration at the mid-point of the cold tower will be lower than that in the hot tower. The direction of shift can easily be remembered by thinking that a high liquid rate in effect washes the D_2O down through the cold and into the hot tower.

In the Dana units, four cold towers and four hot towers are operated in parallel as the first stage. The liquid flows and the gas flows from the four sets of towers are mixed in passing through common liquid heaters and condensers, and are then redistributed to the towers. Not only does this complicate the problem of flow control, but the mixing tends to mask the relationship between hot and cold tower mid-point concentrations.

In practice at Dana, this problem is resolved by adjusting cold tower L/G to maintain a specific mid-column concentration of 0.0190 ± 0.0020 mol per cent D_2O . The hot tower L/G's are then adjusted independently to maintain the same mid-column concentration. In the latter stages, the relations between cold and hot tower L/G are fixed and adjustment

of the cold tower flows to give a mid-column ratio of one is used to maintain optimum control. A control chart is used on which hot and cold tower mid-column and cold tower base concentrations are plotted every 8 hours. This chart is the device by which process flow control is judged and changes in flow are decided upon.

Since each Savannah unit is composed of only one cold tower - hot tower pair in the first stage, the problem is simplified. The mid-column concentrations are maintained equal by variation of the liquid feed flow. Similarly, in the second stage, the mid-stage concentrations (in this case based on a sample taken between the two cold towers compared to a sample taken between the two hot towers), are maintained in the ratio 1.5 to 1 by varying the liquid flow to the second stage. The higher mid-column ratio reflects the concentration effect discussed above.

EFFECTS OF VARIATIONS IN PRESSURES AND TEMPERATURES ON FLOW RATES AND RECOVERY

The pressures and temperatures at which the GS units may be operated have been fixed within fairly narrow limits in the design of the equipment. Variations within these limits can, however, have significant effects on the principal flow rates and the rate of recovery of D_2O by the units. In the course of process design calculations for Dana and Savannah, several cases that involve different combinations of pressure and temperature have been calculated. These serve as a convenient basis for illustration of the effects of these variables.

The Dana units have been designed for certain operating pressures, with extra metal thickness allowed in the shells of vessels so that there will be adequate strength to withstand design pressures even after considerable corrosion of the shells has taken place.

The Dana units were designed to operate with cold towers at $30^{\circ}C$ and hot towers at $120^{\circ}C$. During periods when excess steam is available it is possible to operate these units at somewhat lower steam efficiency but higher production rate by raising the hot tower temperature.

At Savannah, some of the units are lined with stainless steel and can be run indefinitely at pressures that are higher than Dana design. In summer, the Savannah units operate with cold towers at $35^{\circ}C$ because of high cooling water temperatures. They were designed to run with hot towers at $130^{\circ}C$ to compensate for the summer cold tower temperature, conservatively taken as $40^{\circ}C$.

The values of β , liquid-gas ratios, feed rates and recovery rates, for design conditions and current operating conditions at Dana and Savannah River are presented in Table VI.

TABLE VI

EFFECTS OF TEMPERATURE AND PRESSURE
ON OPERATION AND RECOVERY OF A GS UNIT

Note: Flows are for a Dana unit or its
equivalent, i.e., four first-stage
column pairs at either Dana or
Savannah

<u>Case</u>	<u>Dana Design Cond.</u>	<u>Dana Current Cond.</u>	<u>Savannah Design Cond.</u>	<u>Savannah Current Cond.</u>
<u>Temperature, °C</u>				
Cold tower	30	30	40	32
Hot tower	120	135	130	138
<u>Average pressures, psia</u>				
Cold tower	250	270	292	292
Hot tower	268	290	307	313
<u>Ratios</u>				
$\beta_c = 1/m_c$	2.294	2.290	2.220	2.272
$\beta_h = 1/m_h$	1.707	1.585	1.653	1.569
$R_c = L/G_c$	0.481	0.490	0.494	0.492
$R_h = L/G_h$	0.532	0.575	0.552	0.528
<u>Flows, mols/hr</u>				
L_c	23,200	31,850	25,440	35,330
G_c	48,240	65,000	51,530	74,500
L_h	28,400	44,800	32,100	48,490
G_h	53,300	77,900	58,180	90,030
$L_o = \text{feed}$	22,600	31,000	24,770	35,280
<u>D₂O Recovery, mols/hr</u>				
Maximum theoretical*	0.664	1.01	0.692	1.12
Actual at correct L/G	0.543	0.949	0.543	1.03
Recovery as per cent theoretical	82	93.9	78	92.0
Recovery as per cent feed	16.4	20.8	14.9	20.0

* Recovery achievable with an infinite number of theoretical plates
at the given conditions.

A series of cases which will illustrate the effects of pressure, temperature, and flow on production can be developed through the use of the following equation which defines the production rate of a single-stage GS unit.

$$\text{Production (mol D}_2\text{O/Unit Time)} = L_c x_{tc} \left(\frac{Q_c - 1}{Q_c} \right) \left(\frac{Q_c^{N_c} - \frac{x_{bc}}{x_{tc}}}{Q_c^{N_c} - 1} \right) + L_h x_{bh} (Q_h - 1) \left(\frac{Q_h^{N_h} - \frac{x_{th}}{x_{bh}}}{Q_h^{N_h} - 1} \right) \quad (42)$$

This equation has been found to be quite accurate when used for prediction of changes in production that result from small changes in operating conditions. The production rates that are calculated from this equation are, however, approximately 3% lower than are those that are actually achieved in the Dana GS units, which probably reflects uncertainties in tray efficiencies, flow rates, equilibrium constants, and physical properties.

The effects of changes in the several independent variables of GS unit operation, other conditions in each case remaining constant, are as follows:

- (1) Each 1°C reduction of CT-1 temperature, in the range 30-40°C, increases production by 2.5%,
- (2) Each 1°C reduction of CT-2 temperature increases production by 0.3%,
- (3) Each 1°C increase in HT-1 temperature, in the range 120-140°C, increases production by 0.9%,
- (4) Each 1% increase in flow increases production by 1%,
- (5) Each 1% increase in gas quality increases production by 1%,
- (6) Pressure changes do not significantly affect production except as they affect attainable flow, humidity and temperature variables.

ENGINEERING DESIGN

DESCRIPTION OF DANA EQUIPMENT

Flow Diagram

Figure 20, a flow diagram of a Dana GS unit, shows all of the principal towers, heat exchangers, pumps, and gas blowers. The following glossary is given of the symbols that are used to designate these pieces of equipment.

CT - Cold tower	GB - Gas blower
HT - Hot tower	PC - Primary condenser
PT - Purge tower	SC - Secondary condenser
V - Stripper	LH - Liquor heater
CTP - Cold tower pump	SX - Stripper exchanger
HP - Humidifier pump	AX - Auxiliary exchanger
HTP - Hot tower pump	CCD - Condensate drum
CCP - Condensate pump	HTD - Hot tower drum
PTP - Purge tower pump	HD - Humidifier drum
CWP - Cooling water pump	WT - Weigh tank
WTP - Weigh tank pump	VR - Product reboiler
AP - Auxiliary pump	VC - Product cooler
NP - Neutralization pump	

Note: Numbers that follow letters designate the stage, with certain exceptions in the first stage where several pieces of equipment have the same letter designation. In these cases, the number or letter following the equipment nomenclature denotes the individual piece of equipment..

Process feed water that is heated to about 28°C in the Water Treatment Plant is fed at an equal rate to the top of each of the four parallel first-stage cold towers. The heat of solution of H₂S in water raises the water temperature to 34-35°C. Process gas that is cooled to 40-45°C in the secondary condensers enters the bottom of the four cold towers and is cooled further to 33.5°C by the recirculation of a stream of water from the base of the tower, through an auxiliary heat exchanger and back onto the fifth tray. The bottom five trays in the cold towers at Dana are thus used for gas cooling rather than for enrichment.

Effluent liquid streams from the cold towers are combined and pumped through the liquor heaters wherein the liquid temperature is raised to 120°C or higher by heat exchange with effluent from the stripper. Cold process gas is pulled from the top of each cold tower by a centrifugal blower and enters the bottom of the humidifier section of the hot tower. Gas from the top of the hot tower is cooled to the cold tower temperature in the primary and secondary condensers and cold tower recirculation section. This completes the circuit of process gas through the cold and hot towers of the first stage.

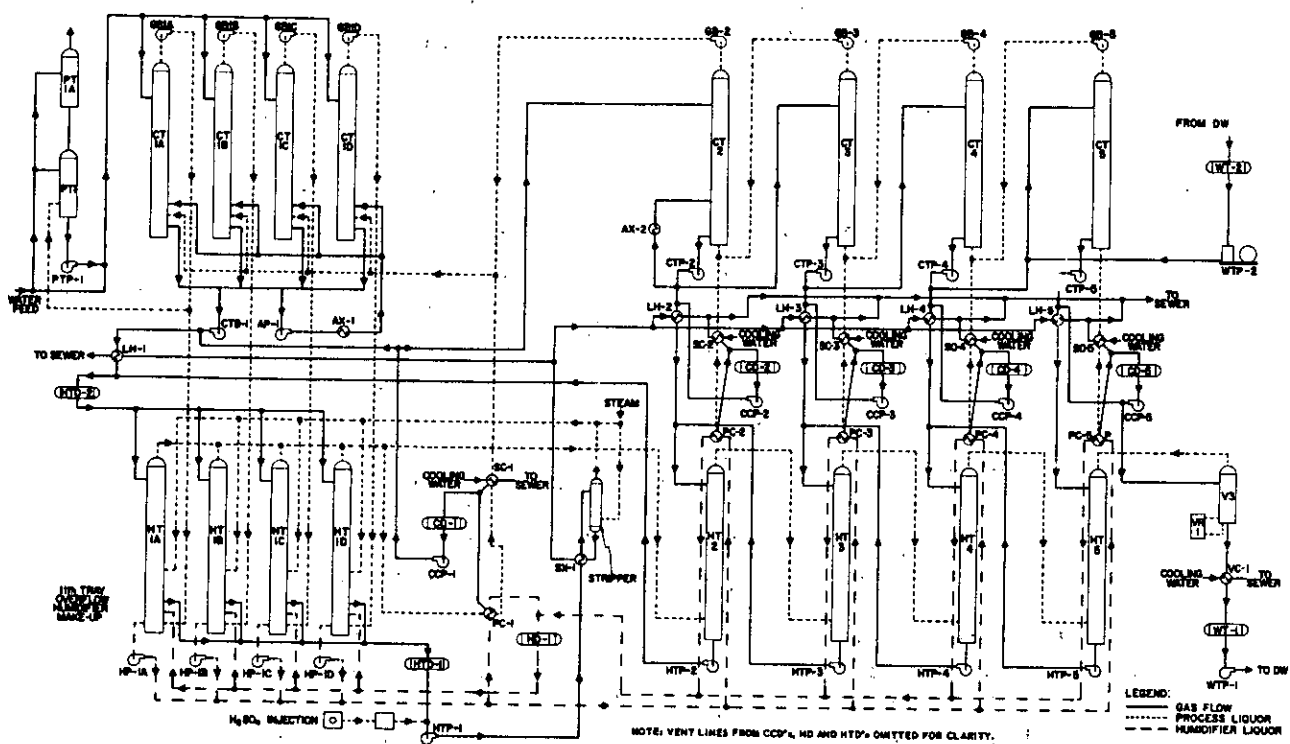


FIGURE 20 - FLOW DIAGRAM OF THE GS PROCESS - DANA UNIT

The bottom ten plates of each first-stage hot tower are used for humidification (they have little effect on D_2O concentration). Gas from the cold tower enters the bottom of the humidifier section and is brought up to near hot tower temperature and humidity by counter-current contact with hot water which is introduced onto the tenth plate of the hot tower (top humidifier plate). The cooled humidifier water is taken from the bottom and pumped through the tube side of the primary condenser where it is again heated to near hot tower temperature by gas from the hot tower. This exchange of heat represents the first step in cooling the gas that leaves the hot tower, before it is introduced into the cold tower. The gas leaves the primary condensers at about $75^{\circ}C$ and is cooled further to $45^{\circ}C$ by cooling water in the secondary condensers, and finally is cooled to CT temperature in the recirculation section of the cold towers.

The gas that has passed upward through the ten trays of the humidifier section is saturated to 85-90% with water vapor and is somewhat below the desired hot tower temperature. Additional heat and water vapor is supplied by introducing steam (carrying some H_2S) from the top of the waste stripper into the hot tower between the 11th and 12th trays.

The process stream from the hot tower proper (11th plate) is passed through the tubes of the stripper heat exchanger where it is preheated by the hot stripped waste that passes through the shell side. The preheated liquor enters the top of the stripper at about $200^{\circ}C$. The hydrogen sulfide is stripped from the waste by steam that is fed to the bottom of the stripper. The steam, along with the stripped hydrogen sulfide, passes directly from the top of the stripper to the 11th tray of the hot tower. A portion of the steam required to maintain hot tower temperature bypasses the stripper and is fed directly to the hot towers.

The stripped waste, after leaving the stripper heat exchanger passes through the shell side of the liquor heater. The liquid from the cold tower passes through the tubes and is heated to hot tower conditions, thus completing the heat-recovery cycle.

Since the hot gas to the bottom of the second-stage hot tower comes directly from the top of the first-stage hot tower the gas heating and humidification that are required in the first stage is unnecessary. Primary and secondary condensers are, however, needed to cool the gas between the second-stage hot and cold towers. The arrangement is similar to that of the first-stage, and the second-stage primary condenser supplies heat to a portion of the water that circulates in the humidifier.

The gas from the second-stage cold tower rejoins the gas effluent from the first-stage secondary condenser to make up the gas feed to the first-stage cold tower.

A portion of the liquid from the first-stage cold tower in a like manner provides the cold, concentrated liquid feed to the second-stage cold tower. Similarly, liquid from the second-stage hot tower is recycled back to the first stage to join the liquid effluent from the first-stage liquid heater. Stripped waste from the first stage serves as the source of heat for the liquid heaters of the higher stages.

The arrangement of flows and heat exchange on Stage III-V is the same as for Stage II.

A portion of the condensate stream from the fifth-stage condensers is drawn off as product. Condensate is used since it contains relatively little dissolved solids.

Water containing between 2 and 3 mol % D_2O is returned to the GS process from the DW process. The return stream is pumped back into the GS system at the top of the third-stage hot tower where the concentrations match.

The six identical GS units at Dana are arranged in two groups of three units each; the controls and instruments for each group of three units are located in a central control room where there is a control panel for each unit.

Towers

Each GS tower at Dana contains 70 plates at a spacing of 18 inches. The over-all tower height is 125 feet. The top plate of each CT is run dry* to act as an entrainment separator for the gas entering the blowers. The cross-sectional area of the hot towers is approximately 10% greater than that of the cold towers. Tower diameters are given in Table VII. Because of limitations that are imposed by the design of suitable bubble cap trays, diameters below 2-1/2 feet were not feasible.

Each tower has a liquid sampling point at its mid-point except the first-stage HT's, which have the sample point at the 40th tray, which is the mid-point of the stripping section of these towers. The humidifier section (bottom 10 trays of the first-stage towers) contain split flow trays to carry the high liquid loading, i.e., each tray is divided with liquid flow from center to side and side to center in alternate trays.

TABLE VII

GS Process Tower Dimensions - Dana Unit

Stage	I	II	III	IV	V
Cold towers, dia., feet	11	11	6	3½	2½
Hot towers, dia., feet	12	12	6½	4	2½

* The feed water enters on the second tray and there is no exit weir to hold a liquid level on the top tray.

These towers were originally equipped with Type 410 stainless steel bubble cap trays. As these trays failed due to corrosion, they were replaced with Type 304 stainless steel sieve trays. The sieve trays have a lower pressure drop than do bubble cap trays and reduce the power that is consumed by the blowers. The sieve trays are also less expensive than are bubble cap trays.

Heat Exchangers

All heat exchangers at the Dana Plant are vertical, shell-and-tube units with floating heads. The numbers and arrangement of the units vary with stage and service as described below.

Primary and Secondary Condensers

Two primary condenser units are connected in series and, depending on the stage, from one to eight of these pairs are operated in parallel. There are eight pairs, or a total of 16 units in the first stage, four units in the second, and two each in the higher stages. In the first three stages the secondary condensers comprise one to eight units in parallel. In the fourth and fifth stages there are two secondary condensers in series. The number of units and their surface areas are summarized in Table VIII.

TABLE VIII

Primary and Secondary Condensers

Stage	I	II	III	IV	V
Primary condenser, number	16	4	2	2	2
Approx. surface, ft ² each	4155	4155	2270	625	222
Secondary condensers, number	8	2	1	2	2
Approx. surface, ft ² each	4155	4155	2270	625	266

The first- and second-stage exchangers have since startup been partially lined with Type 316 stainless steel to prevent corrosion-erosion of the shells. The tube bundles which were originally carbon steel have been replaced with Types 304 and 316 stainless steel.

Liquor Heaters

Bottoms from the cold towers of all stages are heated to hot tower conditions in the liquor heaters by hot waste liquor from the first-stage stripper heat exchangers. Both the tube and shell sides are two pass. From one to four units comprise an exchanger; multiple units are connected in series. Exchanger sizes and numbers are given in Table IX on the following page:

TABLE IX

Stage	<u>Liquor Heaters</u>				
	I	II	III	IV	V
Unit 201					
Number of exchangers	4	1	1	2	1
Surface, ft ²	4080	4080	960	146	142
Units 202-206					
Number of exchangers	4	2		2	1
Surface, ft ²	4080	1950	240	146	146

Stripper Heat Exchangers

The stripper exchanger for each GS unit is made up of two parallel banks of four units in series. Waste process water from the bottom of the first-stage hot towers flows through the tube side (one pass), and gas-free water from the base of the stripper through the shell side (two pass). In Units 202-206 the total exchanger surface area is 15,000 ft², while in Unit 201 (the first unit constructed) the total exchanger surface area is 21,200 ft².

Auxiliary Exchangers

These exchangers are provided for the first and second stages only. Process water is taken as a side stream from the base of the cold tower, cooled to 30°C in these exchangers, and circulated back to the fifth tray of the cold tower. This provides auxiliary gas-cooling capacity in addition to that furnished by the primary and secondary condensers. The shells and tube bundles of the auxiliary condensers are carbon steel.

TABLE X

<u>Auxiliary Exchangers</u>		
Stage	I	II
Number of exchangers	1	1
Surface, ft ²	4080	240

Gas Blowers

Motor-driven, centrifugal blowers are provided for circulation of process gas through each stage of a unit. One blower is provided for each pair of towers in the first stage and two blowers (one a spare) for each subsequent stage. Blower parts that are exposed to process gas are carbon steel, except the impellers, which are aluminum. The blowers have mechanical shaft seals; the sealing surfaces are carbon

on "Stellite". Design details of the blowers are given in Table XI.

TABLE XI
Gas Blowers

Current Operating Conditions	INGERSOLL-RAND					ELLIOTT		
	1st Stage CUS-20	2nd Stage CUS-20	3rd Stage CUS-12	4th Stage CUS-8	5th Stage CUS-4	1st Stage P40w1	2nd Stage P40w1	3rd Stage P40w1
Inlet pressure, psig	252	242	232	222	212	252	242	232
Disch. press., psig	284	274	264	254	244	284	274	264
Capacity at suction, (actual cfm)	5700	5500	1535	375	97	4735	4530	1640
Speed, rpm	3570	3570	3570	3570	3570	3750	3750	3750
Impeller size	28-1/2"	28-1/2"	27-3/8"	25"*	28"	25"	25"	25-3/4"
Motor-rated hp	800	800	250	100	40	800	800	250 ←
Motor-input hp (current operation)	1100	1050	360	125	70	1250	1200	400 ←

* Note: A 23.5-inch-diameter impeller has been recommended for this service.

Pumps

All principal process pumps are centrifugal. Mechanical seals are used on 70% of the centrifugal pumps; the remainder have water-cooled soft packing.

Spare pumps are provided at all positions except at the secondary condenser cooling water recirculating pump, the inert-gas purge-tower pump, the weigh-tank pumps, and the drain-tank pump.

Variable-stroke plunger pumps are used to meter DW return liquid to the third-stage towers and sulfuric acid to the stripper heat exchangers.

Waste Stripper

A stripper is provided in each unit for removing H₂S from process waste water. The strippers are 10 feet in diameter, 48 feet high, and contain 12 bubble cap trays at a spacing of 24 inches. Each tray is divided in the center with flow of liquid from side to center and center to side on alternate trays. Feed liquor is equally divided

between the two halves and remains separate on the trays all down the column. The vapor flow divides between the two halves depending upon the pressure drop in each half. The top tray is run dry as an entrainment separator.

Purge Towers

Two purge towers are provided for each unit for the removal of inerts from process gas. The primary purge tower is 4 feet in diameter by 30 feet high, packed with 10 feet of 2 inch Raschig rings and is designed to handle 308 mols of process gas in countercurrent contact with 12,500 mols of feed water per hour.

The secondary purge tower, is 10 inches in diameter by 24 feet high, and contains 15 feet of 3/4 inch Raschig ring packing. It removes additional H₂S from the gas that leaves the top of the primary purge tower by countercurrent flow contact with 80 mols/hr of water.

Product Stripper System

Product liquor from the fifth-stage condensate pump is stripped of H₂S in a stripper that is 6 inches in diameter and 25 feet high, packed with 10 feet of 3/4 inch stainless steel Raschig rings. Stainless steel Raschig rings are used in place of ceramic to keep the silica content low in the product feed to the DW process. A 3 by 7-1/2 foot lower section acts as an accumulator for batch hold-up of stripped liquor. The product is accumulated batchwise and cooled in the product cooler as it flows to the product weigh tank.

The stripper has a shell-and-tube reboiler, which has stainless steel tubes. The heating surface area of the reboiler is 55 ft².

The product cooler is a horizontally mounted, jacketed stainless steel pipe.

DESCRIPTION OF SAVANNAH EQUIPMENT

Flow Diagram

A diagram that shows the principal equipment of a Savannah River GS unit is presented in Figure 21. Four of these units comprise a wing and two wings comprise a building. A wing has the same nominal capacity as a Dana unit. A building is operated as an entity with certain facilities being common to the eight units in it. The individual units can, however, be started up or shut down independently.

Process feed water is warmed to about 27°C in wing feed-water preheaters so as to prevent formation of the solid hydrate of H₂S when the water contacts the gas. This feed water is then metered to each of the first-stage cold towers. The temperature of the water is further raised to 33-35°C by the heat of solution of H₂S.

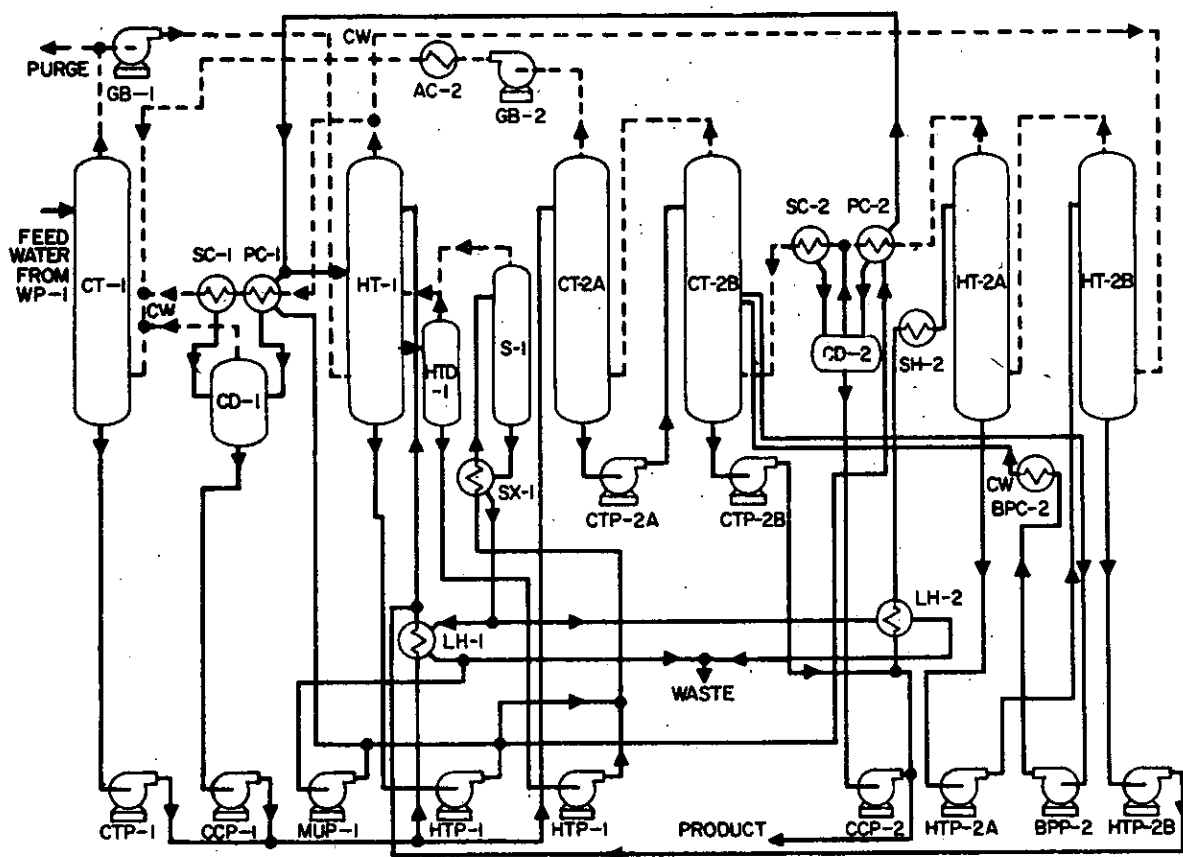


FIGURE 21 - FLOW DIAGRAM OF THE GS PROCESS - SAVANNAH RIVER UNIT

After passing through the first-stage cold towers, the liquid, containing about 0.08% D_2O , is divided into two streams; about $1/3$ goes as feed to the second-stage cold tower and $2/3$ through the first-stage liquid heaters to the first-stage hot towers.

The hot liquid from the first-stage liquid heaters is joined by liquid from the second-stage hot towers and passes down through the first-stage hot tower, leaving at the 11th tray.

Each SRP unit has its own waste stripper; the liquid from the 11th tray of the hot tower is preheated in the stripper heat exchanger, stripped of H_2S by the steam that provides heat makeup to the unit, and after heat recovery, is discarded.

The gas flow through the first stage is similar but countercurrent. Gas from the top of the first-stage cold tower is forced by the first-stage blower through the hot tower, the primary and secondary condensers, and the cold tower. About $1/3$ of the gas from the hot tower is directed to the base of the second-stage hot tower. The gas from the first-stage blower is preheated and humidified in the bottom ten trays of the hot tower before it contacts the main stream of process liquid.

The second stage is flow-wise, a bypass around the first-stage heat exchangers. The two cold towers and two hot towers that are in series in the second stage are operated as if they were one cold and one hot. Liquid from the first-stage cold tower passes through the second-stage cold towers in series, through the second-stage liquid heaters, the hot towers, and back to the first stage. Additional cooling is required near the middle of the second (higher-concentration) cold tower to remove the heat of reaction of HDS forming HDO. The gas stream follows an analogous path from first-stage hot towers, through second-stage hot towers, primary and secondary condensers, cold towers, the second-stage blower and aftercooler, and back to the first stage.

Product that is withdrawn as condensate from the second-stage condensers is stripped of H_2S and is measured in equipment common to the eight units of a building. One purge-gas system also serves eight units. Return from the DW units is metered into one or more units of a building, usually to not more than two.

Towers

All towers contain 70 plates except the second-stage cold towers which have 84 plates and the waste stripper which has 12 plates. The first stage contains one cold tower and one hot tower and the second stage contains two cold towers in series and two hot towers in series. Each first stage has a short tower to strip hydrogen sulfide from the waste water. Descriptive dimensions are shown in Table XII:

TABLE XII

<u>GS Process Tower Dimensions - Savannah River Unit</u>					
Stages	I	I	I	II	II
Tower	Cold	Hot	Waste Stripper	Cold	Hot
Tower height, ft	116	116	28	114	114
Tower diameter, ID, ft	11	12	5	6½	6½
Plate spacing, in.	18	18	20	15	18
Liquid sample points	Middle and base	Middle	Effluent	Base of each tower	Base of each tower
Design pressure, psig	300	300	350	300	300

Primary and Secondary Condensers

The process gas from each hot tower is cooled to cold tower temperature in the primary and secondary condensers. These are vertical shell-and-tube exchangers, with floating heads. Flow on both the shell and tube sides is single pass. In the first stage, two parallel banks of two primary condensers (four exchangers) are followed by two secondary exchangers in parallel. In the second stage, one primary condenser and one secondary condenser are in series. Heat-transfer surface areas are given in the table below:

TABLE XIII

<u>Primary and Secondary Condensers</u>		
Stage	I	II
Primary condenser, number of units	4	1
Approx. surface, ft ² , each	5050	3800
Secondary condenser, number of units	2	1
Approx. surface, ft ² , each	3550	2900

Stripper Heat Exchangers

Waste process water from the bottom of the first-stage hot tower flows through the tube side (one pass), and gas-free water from the base of the stripper flows through the shell side. The exchangers are vertical shell-and-tube units with floating heads. There is one bank of three exchangers in series. The total surface area is 4500 ft².

Liquor Heaters

The liquid from the cold towers of both stages is heated to hot tower conditions in the liquor heaters by hot waste liquor from the first-stage stripper heat exchangers. These exchangers are vertical, single-pass, shell-and-tube units with floating heads. Each stage is equipped with four such exchangers in series. The total area of the first-stage exchangers is 4500 ft² and the total area of the second stage is 1770 ft².

Gas Blowers

Motor-driven centrifugal blowers are provided for circulation of process gas through both stages of a unit. Two blowers are provided, one for the first stage and one for the second. Blower parts that are exposed to process gas are carbon steel, except the impellers, which are aluminum. The blowers have mechanical shaft seals with carbon on "Stellite" sealing surfaces. Design details of the blowers are given below in Table XIV.

TABLE XIV

Gas Blowers

Stage	I	II
Speed, rpm	3600	3600
Motor horsepower	1000	600
Capacity, pound-mols of H ₂ S per hour	13880	4180
Pressure rise across blower, psi	33	54

Pumps

All liquid pumps are centrifugal, except for the variable-stroke plunger pumps which feed DW process return into the GS units. Water-cooled soft packing is used to seal the shafts of all centrifugal pumps of the GS unit proper. The pumps in the product system, however, have mechanical seals with provisions for leakage collection to avoid loss of high-concentration materials. No spare pumps are provided in any position.

Waste Stripper

A stripper is provided in each unit for removing H₂S from process waste water. The stripper is 28 feet high and 5 feet in diameter and contains 12 bubble cap trays on 20-inch spacing. Each tray is divided in the center with cross flow of liquid across each half. Feed liquor is equally divided between the two halves and remains separate on the trays all down the column. The vapor flow divides between the two

halves depending upon the pressure drop in each half.

Purge Towers

Two purge towers in series are provided for each group of six units for the removal of inert gases from the process gas. The primary purge tower is 25 feet high and 5 feet in diameter and packed with 12 feet of 1-inch ceramic Raschig rings. It will handle up to 500 mol/hr of process gas in countercurrent contact with 20,000 mol/hr (700 gpm) of water.

The secondary tower is in series with the primary tower to scrub H_2S from the inerts being vented to atmosphere. It is 18 feet high and 11 inches in diameter and is packed with 15 feet of 1-inch ceramic Raschig rings. The gas is scrubbed with 770 mol/hr (27 gpm) of water.

Product Stripper System

Product (second-stage primary and secondary condenser condensate) is withdrawn from the units and stored in a tank. This liquor is stripped of dissolved H_2S in a column which is 12-3/4 inches in diameter and 24 feet high and is packed with 16 feet of 2-inch-diameter Type 304 stainless steel Raschig rings. A steam-heated reboiler, consisting of a 184 ft² tube-and-shell exchanger, provides boilup. The stripper liquor is cooled in a 206 ft², water-cooled tube-and-shell exchanger and is stored in a weigh tank. A 265 ft² tube-and-shell exchanger reduces humidity of the H_2S being returned to the process. All exchangers are horizontally mounted and tubed with Type 304 stainless steel.

MATERIALS OF CONSTRUCTION

The following summary of materials is given below to present an overall picture of materials of construction. In general, special high quality carbon steels have been used for fabricating the major items of equipment where excess thickness could be allowed for corrosion. Where thin sections were required either Type 304 or Type 316 stainless steel were used although certain substitutions were allowed in specific equipment pieces in order to complete construction in a reasonable time. Type 410 stainless steel in thin sections has been found to be unsatisfactory for use in this process. Type 304 is the lowest-cost grade of commonly available stainless steel which has adequate corrosion resistance where thin (1/8 inch or less) cross section is required.

Materials

Process towers	
Shells, heads, nozzles, bubble caps, plates	Carbon steel Type 410 stainless steel (Replacements of Type 304 stainless steel)
Product stripper shell	Carbon steel
Tank (Drums)	Carbon steel
Primary condensers	
Shells	Carbon steel partially lined with Type 316 stainless steel
Tubes	Types 304 and 316 stainless steel
Secondary condensers	
Shells	Carbon steel
Tubes	Same as primary condensers but with the addition of a complete shroud to provide shell protection in the 1st and 2nd stages
Stripper heat exchangers	
Shells	Carbon steel
Tubes	Type 316 stainless steel
Liquor heaters	
Shells	Carbon steel
Tubes	Type 316 stainless steel
Blowers	
Casing	Carbon steel
Impeller	Type 355 aluminum

The steel that was used for the fabrication of the towers, shells of heat exchangers, and such major pressure vessels was ASTM specification A-212, Grade B "Firebox". This is an especially clean grade of steel having a lower incidence of voids and nonmetallic inclusions than ordinary plate. The plates for use in fabrication of the GS equipment were examined with the aid of the Sperry "Ultrasonic Reflectoscope" to locate voids and cracks.

Plates having large defects were rejected; those having smaller ones were in some cases accepted, but venting holes were drilled from the outside of the vessel to the site of the defect to allow release of any hydrogen.

Minimum thickness holes were drilled in process piping in order to check

the progress of combined erosion-corrosion. These holes are drilled through approximately half the thickness of the pipe and are located at welds and near bends in the piping exit nozzles of vessels. Vent pipes through the insulation have been installed near groups of holes to check for leakage.

To prevent stress induced corrosion and/or cracking, all vessels containing H_2S and H_2S -water solution were stress relieved after fabrication. All field welds were stress relieved in place by electrical induction heating. The maximum tensile stress in bolts used on process equipment flanges was limited to 40,000 psi and all bolts were heat treated to reduce their hardness to a maximum of 27 on the Rockwell C scale. Although bolts are not normally exposed to the H_2S gas, small leaks at flanges leading to high local concentrations of H_2S will result in stress cracking of the bolts unless the above specifications are maintained. Figure 22 shows the relationship between Rockwell hardness and stress which will cause failure of AISI 4140 bolts exposed to the H_2S -water system.

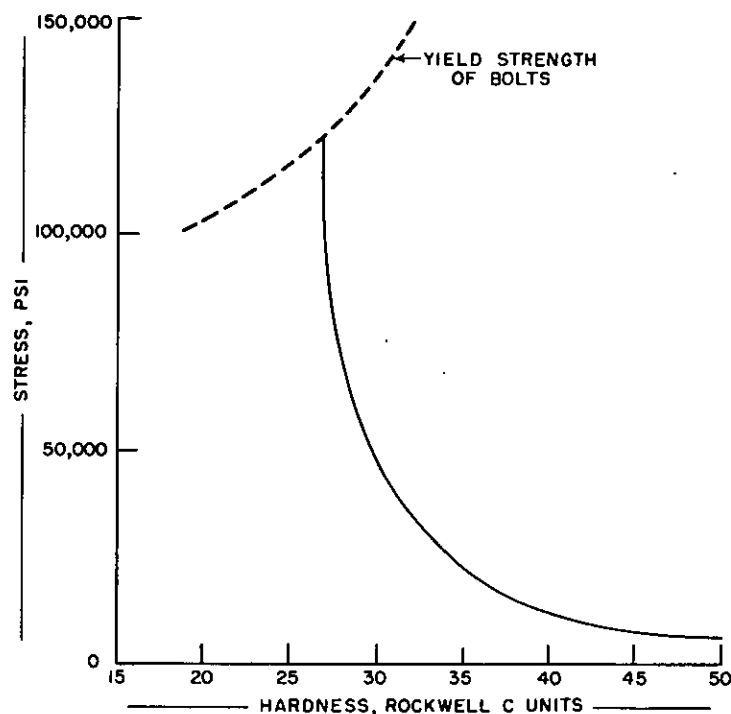


FIGURE 22 - EFFECT OF H_2S ON TENSILE STRENGTH OF AISI 4140 BOLTS

OPERATION

Process Materials

The quality of process streams influences capacity of the GS units and may affect corrosion in the system. It is therefore necessary to place

definite quality specification on make-up gas and feed water in order to ensure GS unit capacity and continuity of operation.

Process Feed Water

Quality of process feed water is important from the standpoint of both production and fouling of equipment. Excessive hardness will result in deposition of scale in heat transfer equipment and towers. High CO_2 content will add inert gas to process gas thereby reducing capacity of the GS unit.

The well water that is used for process feed and cooling at Dana is very hard, containing about 300 ppm of dissolved solids, largely CaCO_3 . The GS process feed water is softened by passing it through ion exchange resin beds. The metallic ions are removed in these beds, and the carbon dioxide that is released passes through the beds and is removed by stripping in vacuum deaerator towers. The technical details of the softening plant are discussed in detail beginning on page 145 of this manual.

The following specifications have been established for treated water.

Hardness	ppm	10 max.
pH		10.5
CO_2	ppm	10 max.
Total solids	ppm	400 max.
NaHS (NaOH)	ppm	150 min.

The river water that is used for process feed and cooling at Savannah, on the other hand, is soft but turbid. The turbidity is normally equivalent to 50 to 100 ppm SiO_2 so that the GS feed water must be clarified. The slight carbonate hardness that is present is readily removed by acidification with sulfuric acid followed by vacuum stripping (deaeration). The feed water, after treatment contains less than 1 ppm turbidity, 5 ppm CO_2 , and 1/2 ppm dissolved oxygen.

Hydrogen Sulfide

H_2S is produced in the Gas Generation area by reaction between sulfuric acid and sodium hydrosulfide. Technical details of the process are discussed in detail beginning on page 85 of this manual.

Briefly, the process consists of reacting an aqueous solution (35-45%) of sodium hydrosulfide (NaHS) with 60% sulfuric acid in a tubular reactor. Products of reaction are separated and the gas is cooled and scrubbed with water. The H_2S is then compressed and condensed, and inerts, such as CO_2 , are vented off. Liquid H_2S is vaporized and sent to the GS units as required.

Typical standards for gas quality are as follows:

% H₂S = 99.0% minimum
% CO₂ = 1.0% maximum

Circulating process gas within the GS units may contain higher concentrations of impurities than does make-up gas. The level of inerts in process gas will depend upon the following factors:

1. The quality and feed rate of make-up gas
2. The quality of feed water
3. The rate of evolution of H₂ by corrosion reactions
4. The rate of purging and the capacity of the purge system for inerts removal

The specification is 98.5% H₂S, minimum.

Waste Disposal

Two basins have been provided at Dana to hold up process waste water in the event that the H₂S concentration in the waste becomes excessive. Each basin provides a six-hour detention period for contaminated water. The basins allow 12 hours of operating time to find and fix H₂S leaks after leakage is detected. After the trouble is corrected, the high-concentration waste in the basins can be bled back into low-concentration waste water at such a rate that the maximum allowable concentration for discharge to the river is not exceeded.

No need for these basins has developed within the five years of operation of the Dana Plant. It has been found that reaction of the waste process water, containing up to 50 ppm of sulfide, with the dissolved oxygen in the waste cooling water with which it is mixed reduces the sulfide concentration to a fraction of a part per million within minutes. Most of the sulfur that is formed in this reaction deposits in the waste stream ditch within a few hundred yards, and does not cause a pollution problem.

The Savannah River Plant has no retention basins. The waste water from all units is combined with cooling water waste and is coursed down an open outfall for a distance of about 2-1/2 miles. The water then mixes with the river in swamp land adjoining the river. The waste water contains less than 1 ppm H₂S and no odor is detectable downstream of the outfall.

Safety

Hydrogen sulfide is a highly toxic gas which is corrosive to eye and respiratory tissues. It has paralyzing effects on lung muscles such that breathing stops quickly following exposure to high concentrations of the gas. In addition to its toxicity, hydrogen sulfide will burn

vigorously and forms explosive mixtures with air within limits of 4.3 to 46% H₂S by volume.

The odor intensities of various concentration of H₂S are as follows:

0.022 ppm	No odor
0.13 ppm	Minimal perceptible odor
0.77 ppm	Faint, but readily perceptible
4.6 ppm	Easily noticeable, moderate
27.0 ppm	Strong, unpleasant, but not intolerable

The effect of hydrogen sulfide on the human body varies with the concentration, as shown in Table XV.

TABLE XV
Toxicity of Hydrogen Sulfide to Men
(National Safety Council)

H ₂ S, %	0-2 Min.	2-15 Min.	15-30 Min.	30 Min. - 1 Hr.	1-4 Hr.	4-8 Hr.	8-48 Hr.
0.005 .010				Mild conjuncti- vitis; respira- tory track irritation			
0.010 .015		Coughing; irritation of eyes; loss of sense of smell	Disturbed respira- tion; pain in eyes; sleepless- ness	Throat irritation	Saliva- tion and mucous discharge; sharp pain in eyes; coughing	Increased symptoms*	Hemor- rhage and death
0.015 .020		Loss of sense of smell	Throat and eye irritation	Throat and eye irritation	Difficult breathing; blurred vision; light shy	Serious irritat- ing effects	Hemor- rhage and death
0.025 .035		Irritation of eyes; loss of sense of smell	Irritation of eyes	Painful se- cretion of tears; weariness	Light shy; nasal catarrh; pain in eyes; difficult breathing	Hemor- rhage and death	
0.035 .045		Irritation of eyes; loss of sense of smell	Difficult respiration; coughing; irritation of eyes	Increased irritation of eyes and nasal track; dull pain in head; weariness; light shy	Dizzi- ness; weakness; increased irritating; death	Death	
0.050 .060	Coughing; collapse and un- conscious- ness*	Respira- tory dis- turbances; irritation of eyes; collapse*	Serious eye irri- tation; light shy; palpita- tion of heart; a few cases of death	Severe pain in eyes and head; dizziness; trembling of extremities; great weakness and death			
0.060 .070 .080 .10 .15	Collapse;* uncon- scious- ness; death	Collapse;* unconscious- ness; death					

* Data secured from experiments on dogs which have a susceptibility similar to men.

The Bureau of Mines^(a) has recommended 20 ppm (0.002%) as the maximum concentration that is allowable for prolonged exposure. It is important to note that at concentrations of 0.01% (100 ppm) or greater the sense of smell is lost. This is an insidious characteristic of the gas, and even lower concentrations cause fatigue of the odor sensory nerves with the result that the exposed person may become insensitive to increases in concentration.

The principal technical effort for protection against the hazard of H₂S is the provision of continuous systems for sampling, analysis, recording, and warning of concentrations of the gas in the environment. Air is sampled continuously at the intakes of building ventilation systems and at a number of representative locations that surround the GS and gas-generation areas. The sample streams are monitored by continuous analyzers that are sensitive to a few parts of H₂S per million of air. The analyzers are equipped with alarms and those on the building ventilation systems will shut those systems down if more than permissible H₂S concentrations exist.

PROCESS CONTROL

Standard Operating Conditions

The arrangement of the process is such that the pressure and temperature conditions that were established for the first stage define most of the conditions of operation for the latter stages. Operating temperatures will hold within the same range for all stages while the pressure from stage to stage will depend upon pressure drop through the equipment.

The principal control points that define current (1956) operation of a Dana GS unit are listed in Table XVI. Savannah River Plant conditions are given in Table XVII.

TABLE XVI

Dana GS Process Conditions

		<u>Current</u>	<u>Current</u>
<u>Cold Towers:</u>			
<u>Liquid Feed Rate</u>		<u>Gas Rate Out</u>	
First stage, gpm	285	First stage, scfm, 60°F	103,600
2nd " "	285	2nd " "	103,600
3rd " "	75	3rd " "	26,700
4th " "	17.8	4th " "	6,650
5th " "	5.11	5th " "	1,670
<u>Liquid Feed Temp.</u>		<u>Waste Stripper</u>	
First stage, °C	34	Pressure, psig	290
2nd " "	39	Steam flow to unit, pph	142,100
3rd " "	43	H ₂ S in tails, ppm	0.05
4th " "	41	pH of tails, pH	5-7.5
5th " "	41	<u>Purge Towers</u>	
<u>Gas Inlet Temp.</u>		Liquid feed primary, gpm	400
First stage, °C	41	" " secondary, gpm	20
2nd " "	41	Inerts flow secondary, scfm	1-2
3rd " "	40	<u>Product Stripper</u>	
4th " "	40	Feed rate, pph	As required
5th " "	40	Draw-off rate, pph	125
<u>Mid-column Temp.</u>		Tails temperature, °C	27
First stage, °C	30	H ₂ S concentration, ppm	0.05
2nd " "	30	D ₂ O concentration, %	15-16
3rd " "	40	<u>Circulating Gas</u>	
4th " "	40	H ₂ S, %	98.5
5th " "	40	<u>Feed Water</u>	
<u>Hot Towers</u>		pH	10.5
<u>Liquid Feed Temp.</u>		CO ₂ , ppm	20
First stage, °C	124	Hardness, ppm	2.0-3.0
2nd " "	100	Total solids, ppm	400
3rd " "	84	NaHS or NaOH, ppm (NaHS)	150
4th " "	80	<u>Cooling Water</u>	
5th " "	85	Chlorine residual, ppm	0.1
<u>Gas Temp. (16th Plate)</u>		On all units not returning cooling water to WT	
First stage only	135	<u>Primary Condenser</u>	
<u>Humidifier Section</u>		Inlet pressure	
Circulation rate, gpm*	1100	First stage, psig	270
Water make-up " *	--		
Purge rate " **	150		

* per tower

** total

TABLE XVII

Savannah River GS Process Conditions

		<u>Current</u>			<u>Current</u>
<u>Cold Towers:</u>					
<u>Liquid Feed Rate, gpm</u>			<u>Humidifier Section</u>		
First stage		320	Circulation rate, gpm		1,200
2nd "		85	Water make-up "		33
<u>Gas Rate Out, scfm at 20°C</u>			Purge rate "		13
First stage		145,000	<u>Primary Condenser</u>		
2nd "		30,400	Inlet pressure, psig		
<u>Liquid Feed Temp., °C</u>			First stage		290
First stage		36	<u>Waste Stripper</u>		
2nd "		35	Pressure, psig		300
<u>Gas Inlet Temp., °C</u>			Steam flow to unit, pph		32,000
First stage		35	H ₂ S in tails, ppm, max.		2
2nd "		35	<u>Purge Towers</u>		
<u>Mid-column Temp., °C</u>			Liquid feed primary, gpm		600
First stage		32	" " secondary, gpm		27
2nd "		40	<u>Product Stripper*</u>		
<u>Hot Towers</u>			Feed rate, pph		As required
<u>Liquid Feed Temp., °C</u>			Draw-off rate, pph		" "
First stage		125	Tails temp., °C		35
2nd "		120	H ₂ S concentration, ppm		0.05
			D ₂ O concentration, %		15-16
<u>Hot Towers</u>			<u>Circulating Gas</u>		
<u>Gas Temp., °C (16th plate)</u>			H ₂ S, %		99
First stage only		138			

* One for each 8 units

Temperature and Pressure Control

Temperatures and pressure changes affect the process by changing solubilities, humidities, and relative volatilities and through them the liquid-vapor phase distribution constant. Solubility and humidity changes affect the relationship between the hot and cold tower liquid-gas flow ratios. Thus, a change in pressure or temperature from standard conditions will change the slopes of the equilibrium and operating lines, resulting in different optimum flow ratios.

The effects on unit performance of variations in pressure and temperature within at least the initial operating limits have been discussed previously in this Manual on page 60, and some figures for representative combinations of conditions were presented in Table VI, page 59.

In general, maximum production will be obtained by operating the GS units at the maximum pressure that is permissible when the actual strengths of vessels and piping are considered. This pressure will decrease through the operating life of the equipment as corrosion proceeds. The cold tower temperature should be held just high enough to avoid hydrate formation (the lower limit being about 29°C). The hot tower should be operated at the maximum temperature that can be achieved with the steam and heat transfer capacity that are available.

Unit pressure is controlled at the primary condenser of the first stages by periodically adding H₂S to make up for loss of gas resulting from

- (a) Process gas dissolved in the waste stream
- (b) Process gas dissolved in final product
- (c) Process gas and inert gas vented from the purge towers
- (d) Leakage of process gas from valves, flanges, pumps, blowers, etc.

With the unit pressure controlled at the first stage, the pressure in subsequent stages depends upon the pressure drop in process lines between stages. The pressures at the primary condensers will be about as follows, varying somewhat with interstage gas and liquid flow rates:

	<u>Pressure, psia</u>	
	<u>Dana</u>	<u>Savannah</u>
First stage	285	302
Second stage	273	281
Third stage	266	-
Fourth stage	261	-
Fifth stage	255	-

Unit pressure is adjusted on an intermittent basis by manual operation of the make-up gas valve from the control room.

Flow Control

Accurate flow control is the key to efficient operation of the GS process. For a given set of operating conditions of temperature and pressure, there is only one ratio of gas to liquid flow that will result in maximum production. Attainment and maintenance of this optimum flow ratio will depend upon, (a) the inherent precision of the

flow control instruments, (b) reliability of performance of the instruments, (c) the operator's setting of the instrument flow control point, and (d) quality of process gas. Pressures and temperatures must be held constant since these affect both the value of the optimum ratio and the indications of the measuring instruments. Effects of changes in flow ratio are shown in Figure 19, page 56.

Criteria for Adjustment of Flows

The flow rates in the GS units are limited by the hot tower gas flow. The proper method of operation, therefore, is to maintain this gas flow at the maximum allowable for the pressures and temperatures existing and to manipulate the liquid flow so as to obtain maximum production. It is not possible, in practice, to predetermine and measure temperatures, pressures, and flows with an absolute accuracy that is sufficient to achieve an optimum recovery. It is necessary, therefore, to hold constant all process variables but one, which for practical reasons is the liquid flow, and then find the optimum liquid flow by analyzing concentration performance of the towers at various liquid flow rates.

The optimum liquid rate is that rate which achieves maximum production of heavy water. When the optimum liquid rate, and therefore optimum flow ratio, is established in a hot-cold column pair the net transport of product toward the high concentration end, the "work done", will be the same in each tower*, and there will be a symmetrical pattern of heavy water concentration gradients in the pair**. It is the latter condition that forms the basis for the best indication of operating efficiency. Referring to Figure 18, page 54, it can be seen that lowering the L/G below optimum (18b) shifts the x-intercepts of the operating lines to the left. This shift is required and inevitable if the end concentration is maintained with the nine plates provided. In the illustration that is given in which the cold tower operating line is parallel to its equilibrium line, the cold tower operating line has had to shift so far to the left, in order to achieve the required concentration gain in nine plates, that the intercept is negative. Offsetting this, but not completely, is the effect on the hot tower. The increased angle between hot tower operating and equilibrium line permits the required concentration gain in nine plates with a smaller initial spread (first-plate gain). This in effect shifts the hot tower x-intercept to the left. The "work done" in the hot tower is thus increased, but not sufficiently to compensate for the cold tower decrease.

As has previously been pointed out on page 56, under first-stage design conditions, when a tower is operating properly, about 20% of the total change in heavy water composition that is attained in the tower occurs between the low composition end and the mid-point.

* See Equation (25), Page 42

** See Figure 18, Page 54

Applying this criterion to a cold tower, we can say that if more than 20% of the total rise has occurred in the top half of the tower, the liquid flow is on the low side of the optimum. Conversely if less than 20% of the total rise has occurred in the top half, the liquid flow is on the high side of optimum. In case of a hot tower, 20% of the total change in composition should occur in the bottom half of the tower. If more than 20% takes place there, the liquid rate is too high; if less than 20% the rate is too low.

If a single pair of towers is being operated as an independent unit (as in a Savannah first stage) it is only necessary to find and fix the optimum flow in one tower of the pair, since this automatically fixes the flow in the other tower. The problem is complicated in the first stage at Dana, however, because each first stage contains not a single pair but four pairs of towers connected in parallel. The 20% rule is helpful in this latter situation.

Sensitivity and Stability

The mid-column concentrations are extremely sensitive indicators of changes in flow. In a Savannah River unit the effect of a 0.5% change in flow rate of the gas or liquid stream is readily seen in the graphical record of mid-stage concentrations that is maintained for each unit. Changes of this magnitude are the normal adjustments that are made to keep ratios at optimum. The adjustments are necessary only infrequently, at intervals of one to several days for normal operation.

H₂S GAS GENERATION

Twelve hundred tons of hydrogen sulfide gas was required initially to charge the GS process units at the Dana and Savannah River Plants. This gas was supplied by generating units which were constructed at each site. The design capacity of each of these units was specified as 15 tons of H₂S gas per day. Liquefaction facilities and storage tank capacity for 200 tons of liquid H₂S were also provided with each generating unit to accommodate the large quantity of gas stored during initial startup and during the GS unit hydrostatic test periods.

PROCESS DESCRIPTION

SELECTION OF PROCESS

Hydrogen sulfide can be manufactured using either primary or secondary starting materials. The primary processes use such naturally occurring materials as barium sulfide, sulfur, or sour natural gas, and produce H₂S respectively by reaction with an acid, catalytic reaction with hydrocarbon fuel, or scrubbing with a suitable absorbent. The H₂S produced by these processes usually contains relatively large quantities of gaseous impurities which make it unsuitable for use in the GS process without further purification.

Secondary processes are based upon synthetic starting materials of controlled composition which produce a high purity product. Such a material is sodium hydrosulfide, (NaHS), which was chosen as the raw material for the gas generation process. The process is based upon the reaction of sodium hydrosulfide with sulfuric acid to release hydrogen sulfide gas.

PROCESS CHEMISTRY

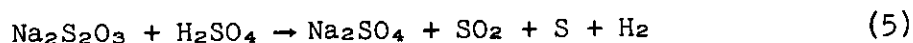
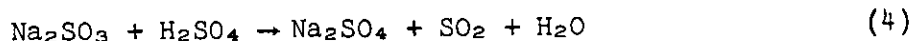
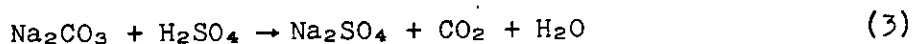
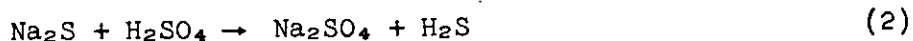
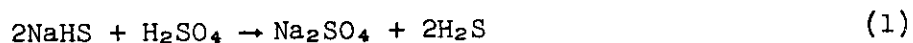
Sodium hydrosulfide is manufactured commercially as a 40% aqueous solution by absorption of H₂S in sodium hydroxide (NaOH). The principal impurities are; sodium sulfide (Na₂S) resulting from incomplete reaction of the NaOH; sodium sulfite (Na₂SO₃), sodium thiosulfate (Na₂S₂O₃), and sodium sulfate (Na₂SO₄) resulting from oxidation reactions during processing; sodium carbonate (Na₂CO₃) originating as an impurity in the NaOH or through the absorption of carbon dioxide (CO₂) from the air; and sodium chloride originating as an impurity in the NaOH. A typical analysis of commercial sodium hydrosulfide is given in Table XVIII.

TABLE XVIII

Typical Analysis of Commercial Sodium Hydrosulfide
(Barium Reduction Company)

<u>Constituent</u>	<u>Weight Per Cent</u>
NaHS	36-40
Na ₂ S	1.0
Na ₂ S ₂ O ₃	0.6-0.8
NaCl	0.6
Na ₂ SO ₄	0.1
Na ₂ CO ₃	0.35
SiO ₂	0.01
CaO-MgO	trace
Fe ₂ O ₃	0.005

Concentrated sulfuric acid (55 to 60° Baume') is used to release the H₂S from the sodium hydrosulfide since it is the least expensive commercial acid and contains no gaseous impurities. The principal reaction and the side reactions that occur in this process are shown in equations (1) through (7).



The sodium sulfide present in the NaHS solution, although not a true impurity, reduces the yield of the process [see equation (2)] and, even more important from an operating standpoint, raises the freezing point of the NaHS solution (see Figure 23) making it necessary to keep the temperature of the NaHS storage tank, and all lines containing the NaHS solution, above 30°C.

Equations (3) through (7) result in the formation of carbon dioxide and free sulfur, both of which are undesirable by-products. The carbon dioxide is an inert gas diluent in the GS process units, and although means are available both in the gas generating unit and the GS units for removing inert gases, CO₂ is particularly difficult to separate

without excessive H_2S losses. The formation of free sulfur, although having no effect on gas quality, can become a serious operating problem within the gas generation unit since it can foul column packing and heat exchange surfaces, and plug the smaller pipelines.

Based upon the percentages of impurities shown in Table XVIII and the reaction shown in equations (3) through (6), the stoichiometric quantities of CO_2 and sulfur produced per ton of H_2S generated are 33 and 46 pounds, respectively. An additional source of sulfur is available through the oxidation of H_2S by sulfuric acid [equation (7)], however, operation of the generating unit with a slight excess of NaHS to maintain an alkaline process pH (H_2S -free) results in a negligible rate for this reaction.

The gas produced by the generation unit is about 98% H_2S ; the balance being carbon dioxide and a small amount of hydrogen generated by the corrosion of the process equipment. The hydrogen and about 50% of the carbon dioxide can be removed during the liquefaction step in the process, resulting in a final gas quality of about 99.3% H_2S .

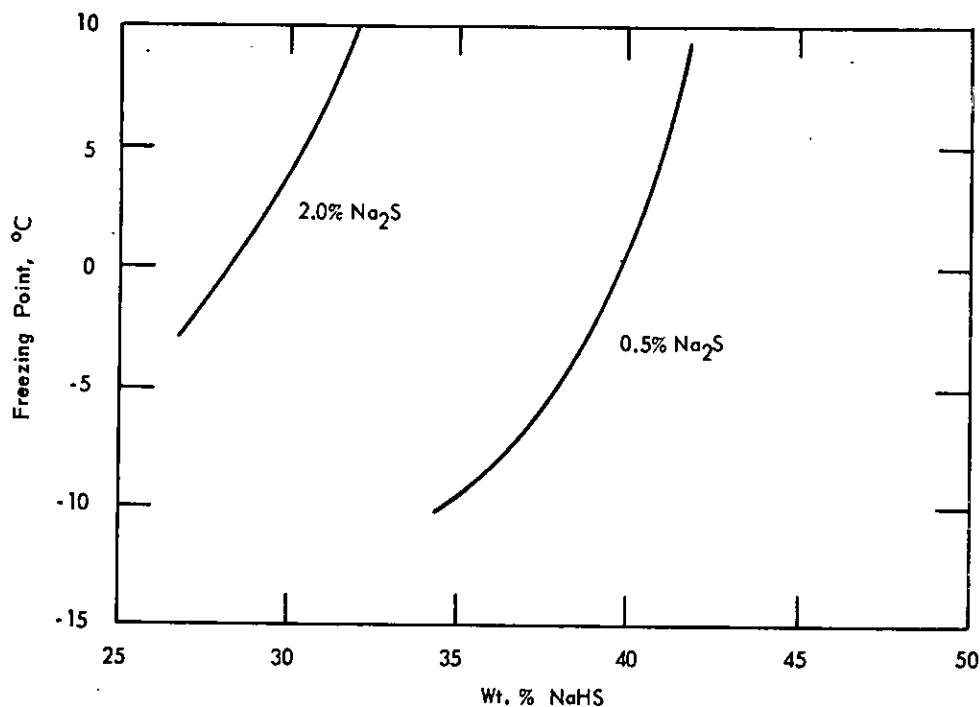


FIGURE 23 - FREEZING POINT OF AQUEOUS NaHS SOLUTIONS CONTAINING Na_2S

Complete thermodynamic and compressibility data on hydrogen sulfide are shown in Figures 24 and B-3, respectively.

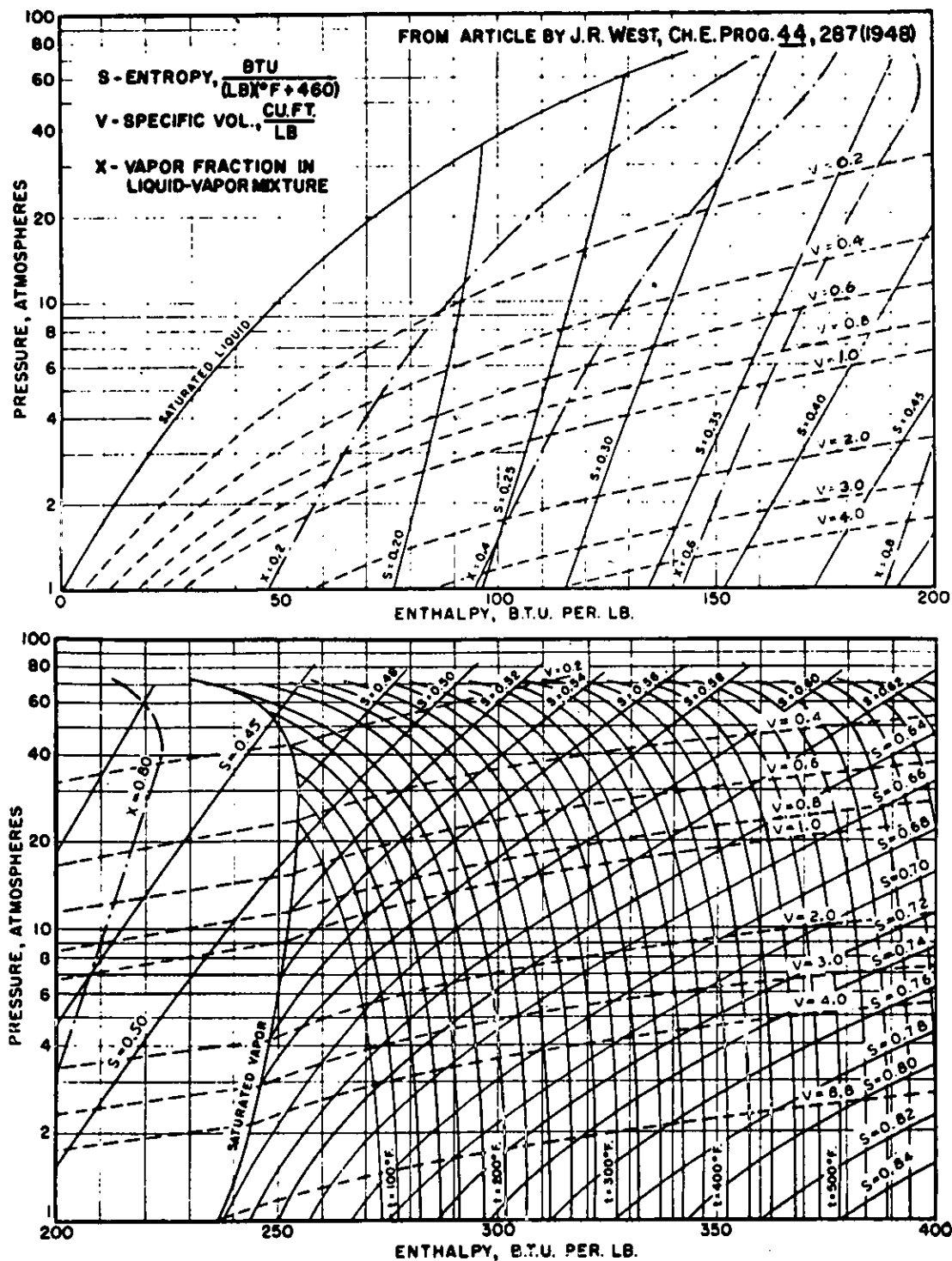


FIGURE 24 - THERMODYNAMIC PROPERTIES OF HYDROGEN SULFIDE

Vapor pressure and density are given in Figure 25, including the pressure and temperature conditions necessary to the formation of the solid $\text{H}_2\text{S} \cdot 6\text{H}_2\text{O}$ hydrate. Discussions of the physiological and corrosive properties of hydrogen sulfide appear respectively on page 78, and 22 of this Manual, and additional physiochemical data can be found in references (10) and (11) listed in the Bibliography.

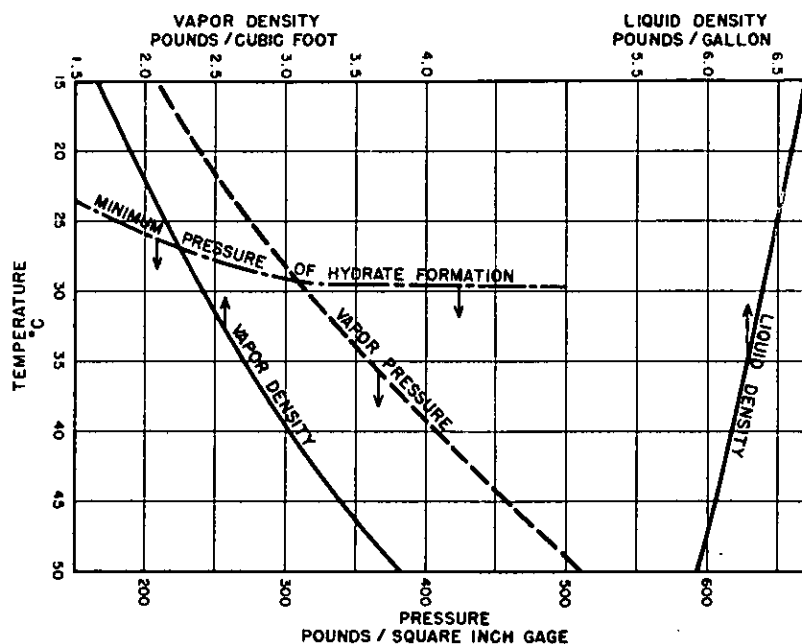


FIGURE 25 - DENSITY AND VAPOR PRESSURE OF HYDROGEN SULFIDE

PROCESS DESIGN

A schematic process flow diagram of the H_2S gas generating unit and associated storage and liquefaction facilities is shown in Figure 26. The equipment arrangement is identical for both the Dana and Savannah River Plants and each has a rated capacity of 15 tons of H_2S per day. The generating unit at Savannah River is currently operating four to five days each month to supply the 30 tons per month of gas make-up required by the Savannah GS units.

Sulfuric acid and sodium hydrosulfide are received in tank car lots and pumped into storage tanks. From the storage tanks, they are metered continuously to a "U" shaped, glass-lined pipe reactor where they mix to form the H_2S . A water stream is also metered to the reactor as a diluent to prevent precipitation of the by-product sodium sulfate. The acid and sodium hydrosulfide streams are automatically adjusted to maintain the pH of the H_2S -free effluent between 9 and 10.

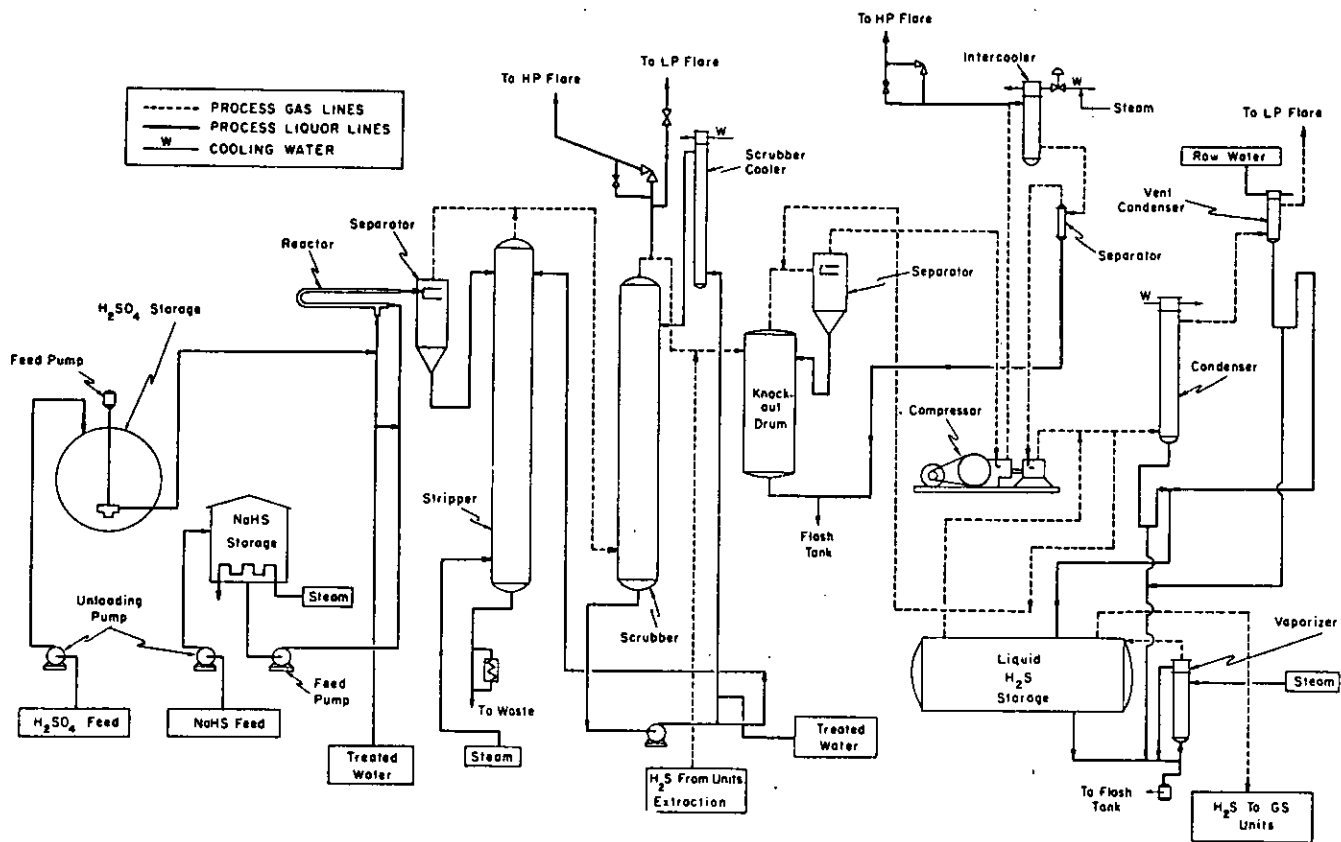


FIGURE 26 - H₂S GENERATION PROCESS FLOW DIAGRAM

Gas and liquid are discharged from the reactor into a cyclone separator from which the liquid flows to a lead-lined packed column to be stripped of dissolved H_2S by steam before being discharged to the sewer. Gas from the reactor separator, combined with the overhead gas from the stripper, passes to a packed scrubber column where it is cooled from 50 to 20°C by recirculated cooling water. Gas discharging from the scrubber passes through a knockout drum and second cyclone separator where entrained water is removed, and from the separator it passes to the suction of a two-stage reciprocating compressor. Water removed from the gas in the scrubber, knockout drum, and separator is pumped to the stripper for disposal to the sewer.

Compressed, heated gas from the first compression stage passes through an intercooler and separator and then to the second compression stage from which it is discharged at approximately 425 psig. The compressed gas is liquefied in water-cooled condensers and piped to storage tanks where it is held under pressure until required by the GS units. The storage tank pressure is maintained by an external steam heated vaporizer having sufficient capacity to deliver 6 to 7 tons of H_2S per hour to the GS units.

Inert gases formed in the reactor cause a buildup of the condenser system pressure and retard liquefaction by blanketing part of the condenser tube surface. These inerts are vented from the main condensers to the low pressure flare stack through a small reflux condenser which reduces the H_2S losses.

H_2S can be returned from the GS units to the gas generation unit for storage. This gas is cooled in the scrubber, passed through the knockout drum and separator to remove water, compressed, liquefied, and transferred to storage.

EQUIPMENT DESCRIPTION

The equipment used in the generation unit and the gas storage facilities at Savannah River is described as follows; that at Dana is very similar. A brief discussion of materials of construction and corrosion has also been included.

GAS GENERATION FACILITIES

The gas generation facilities consist of the following major items of equipment:

Reactor

- Two 2-in. IPS by 10-ft long sections of glass-lined pipe in series forming a "U", with a mixing tee at the inlet end.

Reactor separator	- An 18-in. diameter by 4-ft high, rubber-lined, tangential entry cyclone separator.
Stripper	- A 24-in. diameter by 17-ft high lead-lined column packed with 12 ft of 1-1/2-in. ceramic Raschig rings.
Scrubber	- A 24-in. diameter by 15-ft high column packed with 10 ft of 1-1/2-in. ceramic Raschig rings.
Scrubber cooler	- A horizontal shell-and-tube, 4 pass heat exchanger 20 ft long with an effective transfer area of 276 ft ² .
Knockout drum	- A 30-in. diameter by 7-ft high column acting as a water separator.
Entrainment separator	- A 16-in. diameter by 2-1/2-ft high tangential entry cyclone separator.
NaHS storage tank	- A 250,000-gallon vertical cylindrical tank with internal steam heating coil.
H ₂ SO ₄ storage tank	- A 30,000-gallon horizontal cylindrical tank.
Pumps	- The NaHS feed, H ₂ SO ₄ feed, scrubber recirculation, and tank car unloading pumps are all electrically driven; centrifugal, packed pumps have capacities in the 10 to 50 gpm range.

GAS STORAGE FACILITIES

The gas storage facilities consist of the following major equipment:

Compressor	- A two-stage reciprocating compressor with intercooler and separator driven by a 125-hp electric motor. Two units operated in parallel with a capacity of (a) 625 lb/hr, H ₂ S at 5 psig from the reactor, and (b) 4500 lb/hr, H ₂ S at 100 psig from the GS units.
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- | | |
|------------------------|---|
| Compressor intercooler | - A single pass 10-ft long by 22-in. diameter shell-and-tube heat exchanger with an effective area of 420 ft ² . One unit used with each compressor. |
| Intercooler separators | - A 12-in. diameter by 5-ft high tangential entry cyclone separator. |
| Main condenser | - Three 20-ft long horizontal shell-and-tube heat exchangers in series; each shell having an effective area of 1700 ft ² . Units operated in parallel. |
| Storage tank | - Two 11-ft diameter by 48-ft long horizontal cylindrical tanks with a capacity of 35,000 gallons each. Internal steam heating coil in each tank. |
| Vaporizer | - Six-ft vertical steam heated shell-and-tube calandria having an effective transfer area of 60 ft ² . One for each storage tank. |

MATERIALS OF CONSTRUCTION

Low carbon steel is used throughout the unit for process vessels and piping except where severely corrosive mixtures of H₂S and H₂SO₄ may occur; that is, in the reactor, reactor separator, and stripper. In these locations lead-, rubber-, or glass-lined steel, "Hastelloy" steel or "Haveg" carbon ceramic is used. Stainless steel, Type 304 and 316, is used where thin-walled sections are required such as in heat exchanger tubes, and where corrosion free mating surfaces are necessary in valve assemblies and pumps. For a complete discussion of the corrosion, erosion, hydrogen embrittlement, and blistering, which occur in the H₂S-H₂O system, see pages 22 through 25 of this Manual.

PROCESS CONTROL

GAS GENERATION UNIT PROCESS CONDITIONS

The operating conditions for the Dana gas generation unit shown in Table XIX are illustrative of those used in both plants.

TABLE XIX

Gas Generation Process Conditions

	<u>Control Ranges</u>	
	<u>Gas Generation</u>	<u>Gas Rundown</u>
H ₂ S Generation Rate	3 to 15 tons/day	9,000 lb/hr(max.)
<u>Reactor</u>		
NaHS feed temperature	30°C (+10)	----
NaHS feed rate (40% conc.)	6.5 gpm max.	----
H ₂ SO ₄ feed rate (70% conc.)	3.5 gpm max.	----
Treated H ₂ O feed rate	5.5 gpm min.	----
H ₂ SO ₄ feed temperature	20°C (-20, +10)	----
Treated H ₂ O feed temperature	30°C (+5)	----
Exit liquor temperature	48°C (-13, +2)	----
<u>Scrubber</u>		
Exit gas temperature	25°C (max.)	5°C above hydrate
Inlet water temperature	32°C (±10)	32°C (±2)
Inlet water rate	5-40 gpm	5-40 gpm
Exit water pH	4 (min.)	4 (min.)
Differential pressure through column	0.3 psi (max.)	0.51 psi (max.)
Temperature of cooling water at exit of scrubbing water cooler	55°C (max.)	60°C (max.)
Inlet gas temperature	50°C (-15, +5)	120°C (max.)
Exit water temperature	45°C (±10)	107°C (max.)
Base pressure	7 psig (max.)	100 psig*
<u>Stripper</u>		
Off-gas temperature	96°C (min.)	96°C (min.)
Effluent liquor pH	9-10	----
Effluent liquor Na ₂ SO ₄	29% (max.)	----
Steam (25 psig) feed rate	800 lb/hr (±200)	(variable)
Differential pressure	0.5 psi (max.)	0.3 psi (max.)
Base pressure	7 psig (max.)	7 psig (max.)
Exit liquor temperature	120°C (max.)	120°C (max.)
<u>Knockout Drum</u>		
Pressure	0.25 - 7.0 psig	100 psig (max.)*
<u>Compressors</u>		
Interstage cooler gas exit temperature	20°C (±2)	5°C above hydrate
Second-stage discharge pressure	420 psig (max.)	420 psig (max.)
Intercooler water exit temperature	60°C (max.)	60°C (max.)
Suction pressure	0.25 psig (min.)	0.25 psig (min.)
		100 psig (max.)*
Interstage pressure	55 psig (0, +15)	220 ±10 psig
<u>Condensers</u>		
Liquefied H ₂ S temperature	35°C (-5, +10)	36°C (-5, +10)
Cooling water exit	60°C (max.)	60°C (max.)
<u>H₂S Storage</u>		
Tank pressure	460 psig (max.)	460 psig (max.)

* The maximum pressure for rundown gas from the Dana GS units was reduced from 250 to 100 psig after hydrogen blistering of the walls of the scrubber was discovered in the 1956 hydrostatic test. The blisters were vented in the inside of the vessel which lowered its maximum safe operating pressure.

REACTOR CONTROL

The reactor flow rates depend upon the desired gas production rate, yield losses, reactant concentrations, and impurities. Yield losses result from leaks, oxidation in the reactor, decomposition in the compressors, and use of an excess of one reactant. The calculation of reactant flow is simple stoichiometry based on equations (1) through (6) on page 86, and for operating purposes has been reduced to the use of charts and tabular factors for the concentration of reactants and their impurities based upon a unit production rate of H_2S gas.

Water is added to the sulfuric acid stream entering the reactor to keep the concentration of the sodium sulfate by-product below its solubility limit of 30% in the stripper waste solution.

GAS GENERATION PRESSURE CONTROL

Pressure control of the process is a function of the gas generation rate and the intake capacity of the compressors; however, the latter is not controllable but is determined by the design of the compressor and its volumetric efficiency. The system pressure is, therefore, controlled by the H_2S generation rate or synonymously by the reactant feed rate.

The compressors are provided with pressure-actuated stop switches to prevent drawing a vacuum which might draw air into the system, creating an explosive mixture with H_2S . If H_2S must be generated at a rate lower than the normal compressor intake capacity, a portion of the compressor discharge can be recycled to maintain positive suction pressure.

WASTE STRIPPER CONTROL

The pH of the waste stripper controls the ratio of $NaHS$ to H_2SO_4 fed to the reactor. This pH is controlled between 9 and 10, representing a 0.1% excess of $NaHS$ in the feed reactor and 0.01 to 0.02% sulfide concentration in the stripper waste. This sulfide is oxidized by the atmosphere to free sulfur at the waste outfall. Alkaline operation of the system markedly decreases the free sulfur formation in the system thereby preventing serious fouling of packing and heat exchange surfaces.

The steam rate to the waste stripper must be controlled to hold the free H_2S concentration below 5 ppm to prevent atmospheric pollution.

TEMPERATURE CONTROL OF THE COMPRESSED GAS

At the operating pressure of the liquefaction and storage system (350 to 400 psig), H_2S hydrate will form below $29^\circ C$ ($84^\circ F$). Since

water vapor is present throughout this system, hydrate pluggage can occur in the condensers, compressor intercoolers, storage tanks, and transfer lines. To prevent hydrate formation all pipe lines and tanks containing high pressure gas or liquid H_2S are steam heated, and careful temperature control is maintained on the cooling water used in condensers and heat exchangers.

INERT GAS VENTING

In the GS process any gases other than H_2S act as diluents reducing production in direct proportion to their concentration. It is necessary in the gas generation plant, therefore, to remove by-product gases and inerts; primarily carbon dioxide, hydrogen, nitrogen, and sulfur dioxide. These gases accumulate in the condensers where they are periodically vented to the low pressure flare. They are removed through a reflux vent condenser to minimize coincident H_2S loss.

WATER REMOVAL FROM THE STORAGE TANKS

Water accumulates slowly in the liquid H_2S storage tanks as the gas is used by the GS units and is replaced by freshly manufactured gas. This liquid water in the tanks presents a corrosion problem and when present in the H_2S vaporizer seriously reduces the vaporizing capacity. Water being more dense than liquid H_2S is removed by periodic purging from the bottom of the tank and the vaporizer.

ANALYTICAL CONTROL

Analytical control of the process consists of sampling product, reactant, and waste streams to ensure that they remain within specified limits. These analyses and specifications are given in Table XX.

TABLE XX

		<u>Gas Generation</u>	
<u>Sample</u>	<u>Quantity</u>	<u>Frequency</u>	<u>Specifications</u>
NaHS	2-1/2 liters	Each tank car	NaHS - 40% ($\pm 3\%$) Na ₂ S - 4.0% max. Na ₂ S ₂ O ₃ - 0.4% max. Na ₂ CO ₃ - 0.4% max.
H ₂ SO ₄	1 quart	Each tank car	H ₂ SO ₄ - 70% min.
H ₂ S	250 cc pressure cylinder	Once per day	H ₂ S - 99.6% min. CO ₂ and inerts - 0.4% max.
Waste			
Water	8 oz bottle	Once per day	pH - 9 to 10 Sulfate - 29% (Na ₂ SO ₄) max. Sulfide - 50 to 1000 ppm H ₂ S - 5.0 ppm max. (free)

DW PROCESS

The various methods which have been used or proposed for separating mixtures of light and heavy water, and the reasons for selecting the DW process for the intermediate concentration range have been explained in detail on pages 12 and 16 of this Manual. Briefly, the DW process was chosen for both the Dana and Savannah River heavy water plants because of its dependability. The additional capital and operating costs incurred to achieve this dependability were small since the quantity of material handled is only 0.1% of that handled in the first stage of the GS process.

PROCESS DESCRIPTION

DW PROCESS CONCENTRATION GAIN

The DW units were designed to take a D_2O - H_2O mixture containing 10% D_2O from the GS process, and separate this mixture into a concentrated fraction containing 98% D_2O and a dilute fraction containing 3% D_2O . The 3% material was to be recycled to the GS process, and the 98% material forwarded to the electrolytic process for further concentration. Since the GS process was designed to produce a 15% D_2O concentration and the E process was designed for a 90% D_2O feed, the overlap of the DW process design at either end of the range acted as a safety factor for the three-plant complex.

In actual practice, the DW feed concentration ranges from 12 to 17%, the GS return stream from 2 to 6% and the concentrated product to the E process from 90 to 95% D_2O .

THE SERIES-CASCADE DISTILLATION TRAIN

The DW process is a continuous distillation carried out in a train of six columns. This distillation train comprises a rectifying section wherein the concentration of heavy water is reduced from feed composition (10 to 17% D_2O) to overhead composition (2 to 6%); and a stripping section wherein the concentration is increased from feed to tails composition (90 to 95% D_2O). This still train operates at reduced pressures to take advantage of the higher relative volatility of light to heavy water at low pressure.

The Dana Plant DW process consists of six of the smaller towers of the original heavy water distillation plant which was operated at that site from 1943 to 1945. These six columns are arranged in a series cascade of four stages, two columns each comprising the first and second stages, and single smaller columns in the third and fourth stages.

The Savannah River Plant DW process consists of two identical, six-column, five-stage cascades operated in parallel; having about the

same total capacity as the Dana DW unit. The first stage in these units consists of two columns with a single column of smaller size assigned to each of the remaining four stages.

In both plants, all stages are in series, with transfer of D_2O from stage to stage accomplished by returning all condensate from a higher stage to a plate near the bottom of the next lower stage. A stream of liquid from the base of the lower stage equal to the amount of this condensate plus the product drawoff is sent forward to the higher stage. Several feed points are provided in the first stage so that the feed concentration can be matched to the operating column concentration.

FUNDAMENTAL PRINCIPLES OF PLANT DESIGN

The methods used for designing continuous distillation equipment are well known and are described in detail in various chemical engineering texts⁽¹²⁾. For this reason, the subject is discussed here only briefly.

RELATIVE VOLATILITY

As has previously been discussed on page 31, any water which contains both hydrogen and deuterium contains three compounds, H_2O , HDO , and D_2O , existing together in equilibrium concentration. The equilibrium is established very rapidly, so rapidly that for practical purposes all such mixtures can be considered at equilibrium. A chart relating equilibrium composition to concentration of deuterium in water, is shown in Appendix A as Figure A-1. By reference to this chart it can be seen that at low concentrations of deuterium there are present H_2O and HDO , but very little D_2O ; similarly, at high concentrations of deuterium there are present D_2O and HDO but very little H_2O . Only near the middle of the range are both H_2O and D_2O present in appreciable amounts. The effective separation factor for distillation, therefore, is the relative volatility of H_2O and HDO in the low range, and the relative volatility of HDO and D_2O in the high range. For practical purposes these are identical.

In design calculations one may take the numerical value for the relative volatility of H_2O and HDO , and apply it over the entire range of concentration, on the basis of a two-component system. The assumption of a two-component system results in a slight over design near the mid-point of the concentration range where three components (H_2O , HDO , and D_2O) are actually present in appreciable amounts. The difference is not of practical significance, however, in this case. In setting up calculations for the two-component system, it is usual to express the entire deuterium content as mol % D_2O and the entire hydrogen content as mol % H_2O , and all figures herein quoted are on that basis. This is simply a matter of convenience; the relative volatility data take proper account of the fact that HDO is actually a major component of the system.

Raoult's law, which states that the vapor pressure of each component of a solution is proportional to the mol fraction of that component present in the solution, is applicable to the water system. Under conditions of equilibrium, therefore, the vapor composition is related to the liquid composition by the following formula:

$$a = \frac{y(1-x)}{x(1-y)}$$

where a = relative volatility

x = mol fraction of more volatile component in the liquid

y = mol fraction of more volatile component in the vapor

The relative volatility of the water isotopes varies significantly with temperature, and consequently varies with the pressure prevailing in the distillation equipment.

OPERATING PRESSURE

The lower the pressure at which the water distillation process is operated, the greater is the relative volatility, and consequently the smaller is the quantity of heat or the fewer the plates required for a given separation. Practical considerations of equipment design, however, preclude the use of pressures much below 100 mg of mercury absolute, at the top plate of the column. (The more important of these considerations are the pressure drop in the condenser system and the pressure drop across each plate of the column itself.) The DW units are designed to operate with a pressure of 100 mm Hg above the top plate of each stage.

It may be noted that a somewhat higher production can be achieved from the still train by ignoring steam economy and operating at a higher pressure. As the pressure is raised the steam consumption increases by a larger factor than does the productivity of the still train. However, when the DW process is considered as a part of the heavy water manufacturing plant complex, it can be shown that in terms of over-all plant productivity the steam is more efficiently utilized in the GS process.

A significant reduction in the over-all column pressure and increase in separation efficiency might be realized in future installations through the use of suitably designed low pressure drop sieve plates rather than the conventional bubble cap plates.

STILL TRAIN DESIGN

The composition of the material selected to be produced and sent to the E process for final concentration was 98%. It was assumed that

the feed composition for the DW plant would be 10%, thus allowing some leeway to the GS plant which is actually designed to produce 15% material. It was desired that the D₂O content of the weak fraction returned to GS be relatively low, to reduce the quantities of material handled between the two plants.

Given the quantity and composition of product and the composition of the feed, the McCabe-Thiele graphical method was used. Design data known to be applicable to bubble cap columns in this service are:

- (1) a vapor-carrying capacity of $270 \text{ lb}/(\text{hr})(\text{ft})^2$ of column cross-sectional area at 100 mm Hg absolute pressure,
- (2) an over-all plate efficiency of 70%, and
- (3) a pressure drop of 3.5 mm Hg per (actual) plate at the vapor rate given in (1).

In using the McCabe-Thiele method for calculating fractionation of isotopes in water, it is necessary to take into account the fact that the absolute pressure, and consequently the relative volatility, changes from plate to plate. A practical procedure, starting with the composition at one end of a column, is to locate the operating line, then draw a short section of the equilibrium line based on the average relative volatility prevailing in about four actual (three theoretical) plates; then step off three theoretical plates. From this point draw another section of equilibrium line based on a new relative volatility, step off three more theoretical plates, and so on until the number of steps equals the desired number of theoretical plates in the column.

This general method of computation resulted in the selection of certain existing columns for the Dana still train. It was found that these columns would produce the desired amount of 98% D₂O, and at the same time produce an "overhead" or weak fraction containing about 3% D₂O. The latter was considered an acceptable figure for the material recycled to the GS process. A similar McCabe-Thiele method is used to fix the number of plates and staging of the Savannah River DW process.

It may be noted that the DW still train at Dana, made up as it is of columns salvaged from the old plant, is staged somewhat differently than the new still train designed specifically to operate between concentrations of 3 and 98%. The difference is principally in the second stage, which in the Dana DW plant is the same size as the first stage. (In the original plant these units operated in parallel.) The preferred design for a new still train calls for a smaller second stage and a greater total number of stages, and as a net result, a smaller over-all plate area.

FLEXIBILITY OF THE DW PROCESS

An important characteristic of the DW plant is the fact that as the throughput of D_2O is reduced, the train is able to handle a lower feed concentration. For instance, during the startup phase of the GS plant, the DW plant was able to take material containing as little as 1% D_2O , rather than a 10% solution which is required at full D_2O throughput. The 1% solution was separated into a weak fraction containing less D_2O than does natural water (less than 0.015%) and a concentrated fraction containing at least 50% D_2O . Since the E process can also handle lower feed compositions at lower throughput rates, this weaker-than-design material was taken into the E plant and concentrated to full strength.

This flexibility is important for two reasons, (1) during the startup of the GS process it is not necessary to achieve design concentrations in the GS units in order to obtain some production of heavy water, and (2) by holding low concentrations in the DW train at reduced throughput the amount of D_2O held up in the train is lower. In fact, the preferred method of operating the DW unit is to keep the D_2O concentration throughout the still train as low as possible, contingent on the ability of the E process to handle the end product of the train.

Thus at the start of GS operations the overhead fraction from the DW plant had a D_2O content as low as 0.01%, and the material sent from DW to E was as low as 20%. As production of the GS plant increased, and more D_2O was handled by both the DW still train and the E process, the concentration level throughout the DW train built up until at design throughput of D_2O , the composition of the "overhead" product approached the design value of 3%, and that of the "tails" product approached 90%.

CONCENTRATION OF THE OXYGEN-18 ISOTOPE

The oxygen isotope of atomic weight 18 is present in natural water to the extent of about 2 parts for each 1000 parts of oxygen-16, and the distillation process tends to concentrate oxygen-18, as well as deuterium in the tails fraction. The relative volatility acting to separate the oxygen isotopes, however, is much smaller than that acting to separate the hydrogen isotopes. At the design throughput rate, water enters the DW unit with the normal abundance of 0.2 atom per cent oxygen-18 and leaves the final stage with an oxygen-18 abundance of 0.4 atom per cent, a twofold increase. This change in oxygen-18 concentration does not affect the use of heavy water as a moderator.

Appropriate account must be taken of the variation in oxygen-18 content, in selecting and applying analytical methods for determination of deuterium in the DW and E process streams. A general discussion of analytical methods for heavy water is given in Appendix D.

EQUIPMENT DESCRIPTION

Simplified process flow diagrams for the Dana and Savannah River DW units are shown in Figures 27 and 28 respectively, and a brief description of the principal equipment is given in Table XXI.

TABLE XXI

DW Process Equipment

<u>Columns</u>					<u>Reboiler</u>	<u>Condensers</u>	
Stage Number	Number of Columns in Stage	Diameter, ft	Height, ft	Number of Plates*	Nominal Holdup** Gallons	Area, ft ²	Area, ft ²
<u>Dana Plant</u>							
1	2	10.5	81	72	5800	750	6000
		8.0	90	83	4500		
2	2	10.5	81	72	5200	750	6000
		8.0	90	83	4500		
3	1	5.5	77	72	1600	200	1600
4	1	2.5	77	72	350	50	400
<u>Savannah River Plant</u>							
1	2	7.5	80	72	3000	360	4500
		6.0	92	84	2300		
2	1	5.0	78	72	1300	160	2000
3	1	4.0	78	72	800	110	1200
4	1	4.0	78	72	800	110	1200
5	1	4.0	78	72	800	110	1200

* Plate spacing in all columns is 12 inches

** Holdup includes associated calandria and/or condenser

In addition to the equipment shown in Table XXI each stage of a DW unit is equipped with two-stage steam jet eductors which operate off the condenser head space to maintain system vacuum. All gases reaching the jets first pass through ammonia refrigeration units which recover essentially all of the water vapor.

Tanks mounted on scales are provided so that the DW feed, product, and overhead streams can be analyzed and weighed for purposes of inventory and production control.

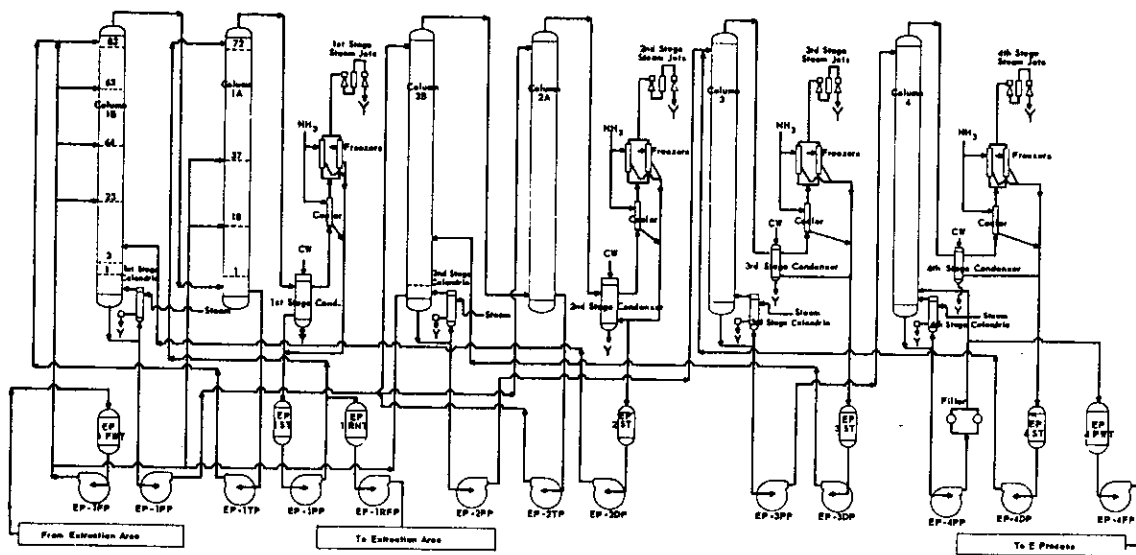


FIGURE 27 - DW PROCESS FLOW DIAGRAM - DANA PLANT

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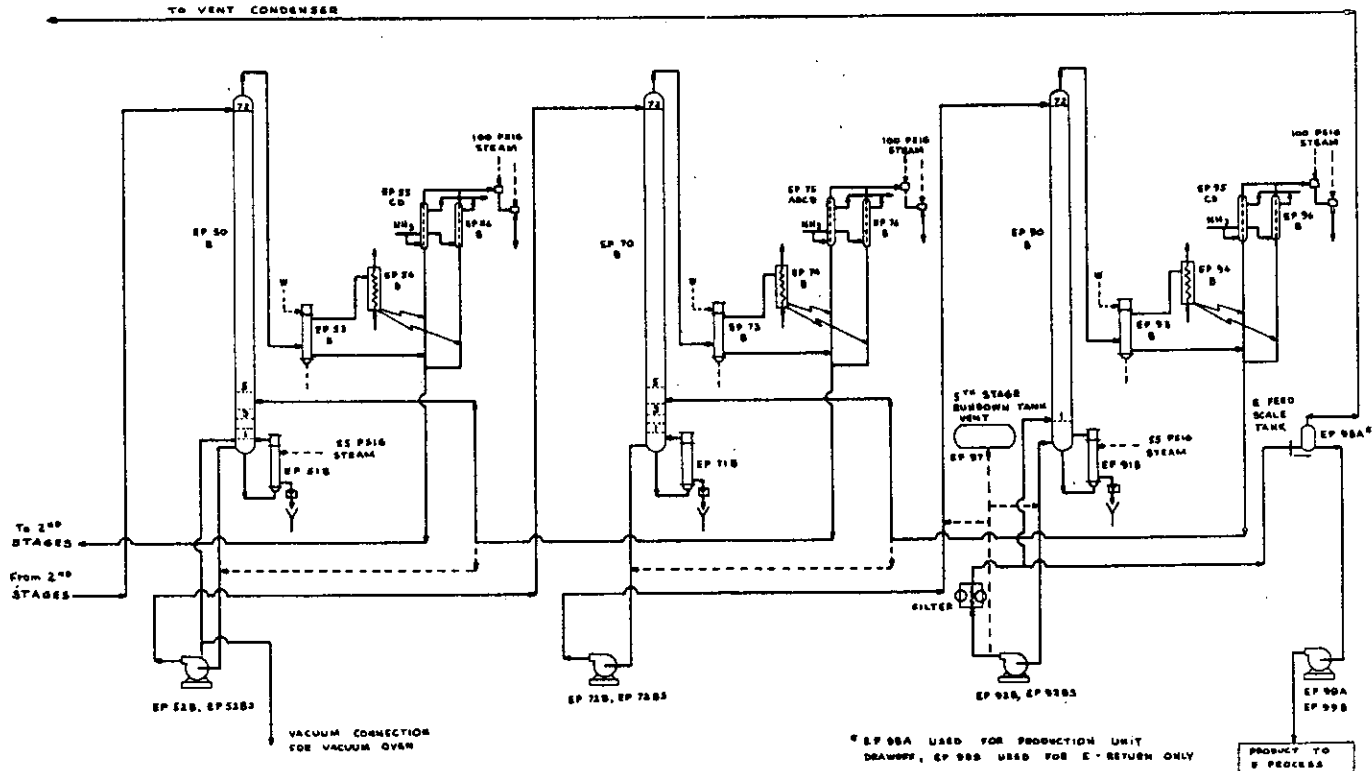
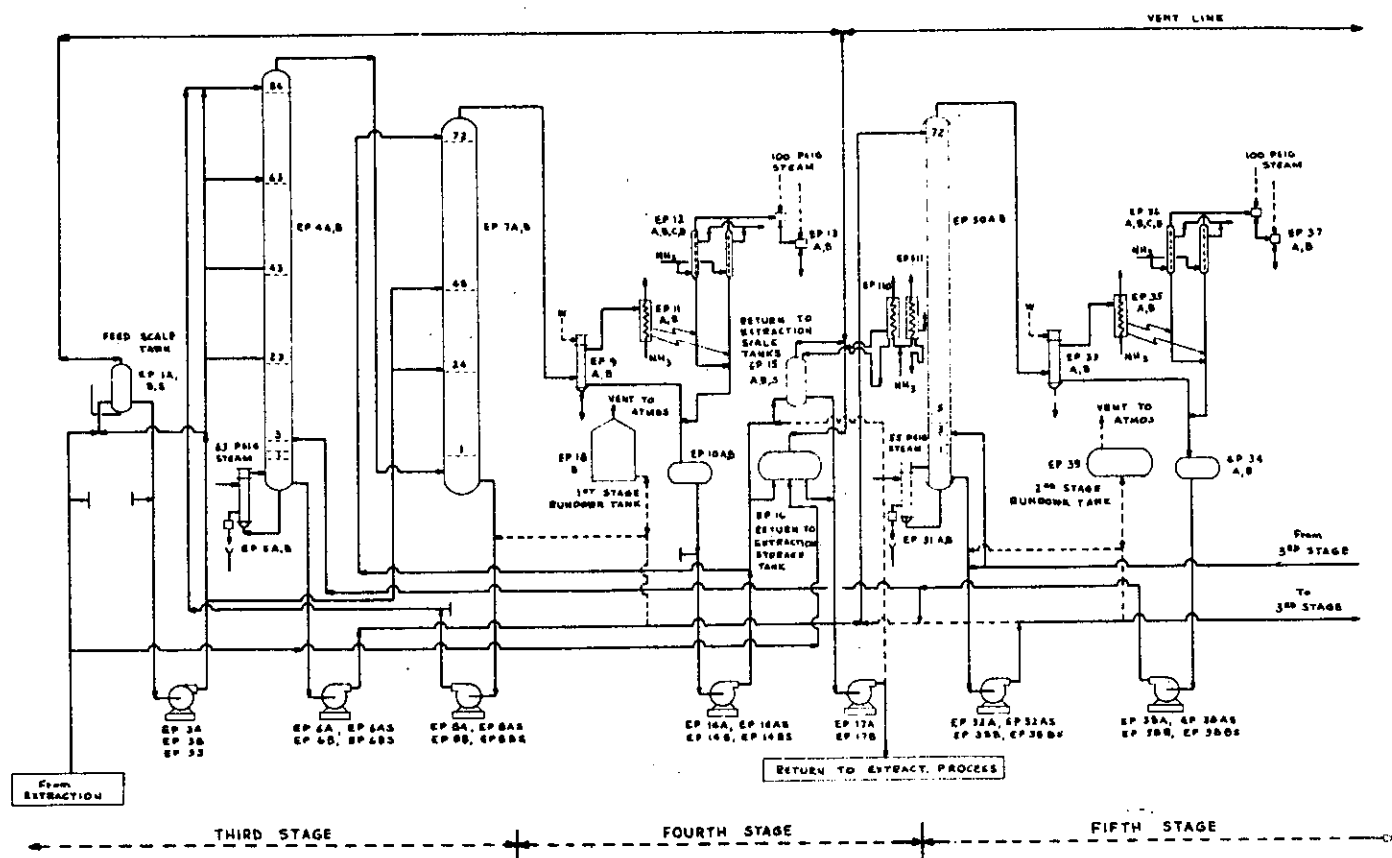


FIGURE 28 - DW PROCESS FLOW DIAGRAM - SAVANNAH RIVER PLANT

PROCESS CONTROL

GENERAL PRINCIPLES

The DW plant is relatively simple to operate. As is the case with any continuous distillation process, flow control is of primary importance, and the more uniformly the various critical flows are maintained the better will be the performance of the still train. The critical flows are:

1. Steam to each reboiler
2. Flow of liquid pumped from base of each tower to next tower in series
3. GS product fed to still train
4. Overhead product withdrawn from still train for return to GS

The problem of operating the DW train is essentially one of balancing flows to and from each tower so that the liquid level in each stays within permissible limits. Because of the characteristics of the system it has proved simpler to do this by flow controllers rather than by level controllers. By this means flows are held constant and levels are allowed to drift slightly to compensate for minor deviations from perfect balance. Slight corrections to flow settings are made as necessary to hold levels within bounds.

A discussion of still train operation logically starts with steam flow. Each column is capable of carrying a certain vapor load and to bring about this vaporization there is required a definite quantity of steam at the reboiler. The first flows to be fixed, therefore, are the steam flows.

The stages of the still train can be started one at a time. The first stage, as previously mentioned, consists of two towers connected to operate as a single column. (All liquid which flows down one tower is pumped from the base of that tower to the top of the second tower, and all vapor leaving the top of the second passes to the base of the first tower.) To start the first stage, sufficient feed is admitted to fill the plates and the reboiler, cooling water flow is established through the condenser, steam is turned on and established at the standard flow for this stage, and all of the condensate from the condenser is allowed to return to the top plate (total reflux). Feed is then started at an appropriate rate. At the same time a flow of "overhead drawoff" is started from the condenser in amount equal to the feed.

To determine whether overhead drawoff rate is exactly equal to the feed rate, it is only necessary to observe the trend of liquid level in the base of the column adjacent to the reboiler. The drawoff rate

is then adjusted slightly to correct any drift observed in this liquid level. Thus the technique of operation consists in setting flows of steam and feed at predetermined values, setting flow of overhead drawoff equal to flow of feed, then making minor adjustments in the flow of overhead drawoff in order to make this flow balance exactly with the feed.

The stage is now operating to concentrate heavy water, and the D_2O content of the material at the reboiler end of the stage will gradually increase.

Assume now that the second stage has been put into operation on "total reflux" in a manner similar to that described for the first stage. The two stages are then connected together by introducing the total flow of liquid from the second stage condenser onto the second plate (counting from base) of the first stage, and at the same time pumping liquid at an equal rate from the base of the first stage to the top of the second stage. These two flows are balanced by observing the level in the base of the second stage and making minor adjustments in the flow of liquid entering the top of that stage. In a similar manner the remaining stages are successively placed in operation.

In normal operation, the total withdrawal of liquid from the train (first stage overhead plus final stage tails) must on the average equal the feed of liquid. The rate of drawoff from the base of the final stage, however, is so small compared to the amount of liquid in the train that variations in this rate of drawoff do not affect, significantly, the problem of controlling the other stages. The withdrawal of product from the final stage can therefore be varied at the operators discretion, the base of the column acting, in effect, as a small, internal, holdup tank for product.

If no product is withdrawn from the final stage, the concentration of D_2O at the base of that stage will gradually increase toward a steady stage value. After withdrawal of product is started the D_2O concentration will level out at some lower value. The composition of the material withdrawn as product from the base of the final stage can be varied over a considerable range simply by varying the total amount withdrawn. As the rate is increased, the D_2O content falls; conversely, as the rate is reduced, the D_2O content rises.

Changes in composition of the "tails" product take place rather slowly because of the relatively large holdup in the still train. In practice, therefore, it is feasible to draw product from the final stage intermittently, observing the trend of D_2O composition in this product and adjusting the amount drawn to maintain the desired product composition.

OPERATING PRESSURE

The preferred range of operating pressure for a DW column is 85 to 95 mm Hg absolute, measured in the condenser vent line. The pressure drop through the vapor line and condenser is about 10 mm Hg so that the pressure above the top plate will be about 95 to 105 mm Hg. As previously noted, operation at a higher pressure will increase the productivity of the still train. This is so because the vapor-carrying capacity of the still columns is directly proportional to the square root of the operating pressure. As the pressure is raised, however, the relative volatility decreases, and the steam consumption increases at a greater rate than does the productivity. As long as the DW train is able to handle its load at 100 mm Hg operating pressure, therefore, nothing is gained, and in fact steam economy is sacrificed by operating at a higher pressure.

As regards operation at pressures below 100 mm Hg it has been stated previously that practical considerations prevent the effective use of pressures much below this figure. It will be noted that as the pressure is reduced, at a constant rate of vaporization, the vapor velocity increases, not only in the column but also in the vapor line and condenser. As velocity increases, pressure drop in the system increases rapidly. For instance, if with design steam flow to the reboiler the pressure at the control point of a DW still column (line between condenser and vacuum jet) is reduced from 90 to 50 mm Hg, the pressure drop between that point and the top plate of the column will rise sharply, and the pressure actually existing at the top plate will be about 75 to 80 mm Hg. The pressure drop across the top few plates of the column also will increase markedly, further reducing the effect of what started as a large reduction in pressure at the condenser vent line. A study of all the variables leads to the conclusion that, although steam economy is favored by reduced pressure, no practical benefits can be achieved by operating much below 100 mm Hg. (The availability, on a commercial basis, of still columns with markedly reduced pressure drop per theoretical plate such as sieve plates would change this situation.)

No mention has been made in this discussion of operating temperatures, normally an important variable in still operation. The differences in boiling point among the water isotopes are so small, however, that the measurement of temperature is of no value in controlling the DW plant.

BOILUP RATES

Column capacity is related to vapor density and vapor velocity by the following formula which has been developed as a design index of capacity. It has been found that operation at "F" factors much above 1.0 results in marked increases in plate-to-plate entrainment with consequent loss of plate efficiency:

$$F = \mu \sqrt{\rho}$$

where μ = vapor velocity, ft/sec (average velocity over column cross section)

ρ = vapor density, lb/ft³

F = index of column capacity

For the columns of the DW plant the design vapor rate was defined by a value for "F" of 1.0. At the design condition of 100 mm Hg pressure the density of saturated water vapor is 0.00564 lb/ft³. By solving for " μ " in the above equation, there is obtained a value for vapor velocity of 13.3 ft/sec. The vapor rate per square foot of area is then 270 pounds per hour.

Experience has indicated that the DW columns will operate at "F" factors above 1.0 with little loss in efficiency since the design "F" factor was based on the conditions on the top plate of each column. Operation at "F" factors above 1.0 decreases the efficiency of only a few of the top plates while the throughput is increased by the higher boilup, throughout the column.

PROCESS LOSSES

Only the bottom of the second column in the first stage, the process pumps and pump discharge lines operate at pressures above atmospheric. Therefore there is very little hazard of product loss in the DW process. However, product dilution can occur through calandria or condenser tube leaks or through air inleakage carrying with it natural concentration water vapor. Product dilution is controlled by periodic fluorescein dye injection on the calandria steam chests and condenser cooling water. Any dye concentration showing up in the process steam is indicative of a leak. Air inleakage is detectable by the closing of a pressure-controlling air bleed which is located in the steam jet suction line (see Figure 27, page 103). Closing of this valve and overload of the ammonia coolers both indicate that there is an air leak in the column with which the jet and cooler are associated.

All tanks or equipment in the atmosphere pressure parts of the feed, tails, or overhead systems where water vapor can escape are protected by passing all of the vents for such equipment through ammonia coolers or desiccant traps.

STANDARD OPERATING CONDITIONS

Table XXII shows the standard operating conditions for both the Dana and Savannah River DW processes.

TABLE XXII

DW Process Standard Operation Conditions

DANA PLANT

Column Head Pressure	Range	Normal
First stage	80-200 mm Hg absolute	100
Second stage	80-200 " " "	100
Third stage	80-200 " " "	100
Fourth stage	80-200 " " "	100
Boilup Rates	Maximum	Normal
First stage	30,000 lb/hr	23,000
Second stage	30,000 "	23,000
Third stage	8,000 "	6,200
Fourth stage	1,700 "	1,200

SAVANNAH RIVER PLANT

Column Head Pressure	Range	Normal
First stage	60-200 mm Hg absolute	90
Second stage	60-200 " " "	90
Third stage	60-200 " " "	90
Fourth stage	60-200 " " "	90
Fifth stage	60-200 " " "	90
Boilup Rates	Maximum	Normal
First stage	16,500 lb/hr	11,000
Second stage	7,900 "	5,000
Third stage	5,000 "	3,000
Fourth stage	5,000 "	3,000
Fifth stage	5,000 "	3,000

E PROCESS

The E process is the final concentration operation in the production of 99.75% pure heavy water. This process follows the separation and concentration of heavy water to 90%, which is accomplished in the GS and DW processes using chemical exchange and distillation, respectively. The E process at Dana and Savannah River are enlarged versions of the batch electrolytic process used for final concentration of heavy water at the Morgantown Ordnance Works during the period 1943 to 1945.

FUNDAMENTAL PRINCIPLES

SEPARATION FACTOR

When water, which is a mixture of the oxides of the hydrogen isotopes, is electrolyzed, the heavier isotope, deuterium, is concentrated in the residue as deuterium oxide while the lighter isotope, protium, is concentrated in the evolved gases. This concentration effect is attributed to the difference in mobilities of the protium and deuterium ions in solution. The separation is analogous to simple batch distillation and can be expressed in terms of the Rayleigh equation; i.e., the relationship between the liquid in the cell and the gas evolved may be expressed as ⁽¹²⁾

$$\ln \frac{A_1}{A_2} = \alpha \ln \frac{B_1}{B_2}$$

where

$$\alpha = \frac{(x_b)(y_a)}{(x_a)(y_b)}$$

when A_1 = total mols or pounds of H_2O in the charge

A_2 = total mols or pounds of H_2O in the residue

B_1 = total mols or pounds of D_2O in the charge

B_2 = total mols or pounds of D_2O in the residue

x_a = mol % H_2O in the cell liquid at any instant

y_a = mol % H_2 in the cell gas at any instant

x_b = mol % D_2O in the cell liquid at any instant

y_b = mol % D_2 in the cell gas at any instant

α = separation factor

The over-all separation factor (alpha) under practicable operating conditions with carbon steel cathodes and nickel anodes is between 8 and 10. Alpha is affected adversely by entrainment and by high cell temperatures, both of which increase the water concentration in the cell off-gas.

ELECTROLYSIS

In order for electrolysis to take place, an electrolyte must be present to carry the current through the solution between the electrodes. The potential required to cause current flow is dependent upon

- (1) the decomposition potential of the water,
- (2) the overvoltage of the gases and polarization of the electrode surfaces,
- (3) the resistance of the electrolyte, and
- (4) the resistance of the power supply connections.

Depending on these four factors, the voltage required for the cell design and electrolyte used in this process ranges from 2.5 to 3.5 volts. The higher the voltage during electrolysis, the greater the heat evolved in the cell; the higher the vaporization rate of the electrolytic solution, and the lower the over-all alpha.

The electrolysis operation is carried out in cells in which no provisions are made for separating the cathode and anode gases evolved. This type of cell is preferred to the diaphragm type, in which hydrogen and oxygen gas are separated, because of its lower power consumption, greater separation factor and general simplicity.

BURNING OF CELL OFF-GAS

To complete the separation process and obtain the dilute overhead material from the cells in a form in which it can be stored for reworking, it is necessary to recombine the hydrogen and oxygen gas mixture. The recombination is done by burning the gas mixture in a water-jacketed chamber. The water formed is condensed and segregated in cut tanks according to its deuterium content.

DEUTERIUM-HYDROGEN EQUILIBRIUM

Deuterium and hydrogen exist in water as the compounds HDO and D₂O. A similar distribution of D is found in hydrogen gas, the molecules being D₂, HD, and H₂. These molecules do not react at ordinary temperatures in the absence of a catalyst. For further discussion of this subject see Appendix A.

PROCESS DESCRIPTION

The E process was designed with ample capacity to process the heavy water extracted and concentrated through the intermediate range by the GS and DW processes. The capacity of the E process, at a 99.75% D₂O product concentration, varies with the concentration of the feed. During normal operation the cells are run at full capacity and the D₂O concentrations between the DW and E processes adjust themselves to

balance the net heavy water throughput of the integrated plant complex comprising GS, DW, and E. This net production is fixed by the GS process, which performs the initial extraction of D_2O from the natural water feed. At maximum production of the GS plant, equivalent to 2800 pounds per day of 99.75% D_2O , the concentration entering the E plant is about 90% D_2O .

As shown in the flow diagram, Figure 29, the feed to the E process from the DW process is first oxidized with potassium permanganate to remove organic impurities and then distilled to remove dissolved solids. Potassium carbonate is then added to this purified material as an electrolyte. As the solution is electrolyzed, deuterium concentrates in the cell residue, and the lighter isotope, hydrogen, is concentrated in the gases evolved from the cells. These gases are burned to water which is condensed, segregated, and reworked according to the per cent deuterium contained. The final product heavy water is cell residue which has been distilled to remove the electrolyte and any remaining impurities.

PREPARATION OF FEED FOR ELECTROLYSIS

Feed from DW contains small concentrations of dissolved and suspended solids and traces of organic materials that must be removed before electrolysis. Feed is transferred from the DW area product tank to the receiving weigh tank in the E building. It is then pumped from the weigh tank either to the crude storage tank or directly to a steam-jacketed Dopp kettle where it is treated with an excess of potassium permanganate to oxidize organic contaminants, and then distilled to a receiving tank through a fractionating column and condenser. Approximately 3.5% $KMnO_4$ by weight is required to oxidize the organics and other impurities in the crude feed, and to ensure an excess of $KMnO_4$ at the end of the treating cycle. Solid potassium permanganate is added to the Dopp kettle in 125-pound lots as required.

During the oxidation step the kettle is operated on a total reflux at a boilup rate of 0.1 to 0.4 gpm for a period of 90 minutes or sufficient time to oxidize all impurities. The boilup rate, indicated on a rotameter, is controlled by varying the steam to the kettle jacket. Completion of the reaction is determined by laboratory analysis of the permanganate demand of the distillate which must be below 1×10^{-5} mg/ml of distillate or an additional 125-pound lot of potassium permanganate is added to the kettle. The treated product is then distilled over to a storage tank at a rate of 0.1 to 0.4 gpm.

When a total of 500 pounds of potassium permanganate has been expended in the Dopp kettle, natural water is added continuously to the kettle and evaporated until the distillate is below 0.03% D_2O concentration. The remaining liquor and solids are then drained from the kettle and discarded.

Purified feed material is pumped from the storage tank to the electrolyte mix tank where potassium carbonate (K_2CO_3) is added, with agitation, to make a cell feed solution containing 6 to 8% electrolyte.

ELECTROLYSIS

The cell feed solution is run by gravity from the mix tank through a header into the bottom of the electrolytic cells. After filling, the liquid levels in the cells are allowed to equalize, following which all cell feed and drain lines are drained to break the electrical connection between the cells and ground. Separate lines are used to fill the cells and to drain the residue from the cells after electrolysis to prevent dilution of the 99.80% D_2O cell residue. The cell charge is limited to 14.5 gallons so that there is sufficient free-board in the top of the cell to prevent excessive carry-over. When starting a run, the DC cell current is first set at 600 amperes and then increased to 1000 amperes as soon as the hydrogen-oxygen flames have been established at the burners (recombiners). Cooling water is supplied to the cell jackets at a rate of 2 to 3 gpm, entering at $15^\circ C$ and discharging at $16-20^\circ C$. Cell cooling is important since the effective separation factor varies inversely with temperature.

At the plant capacity finally reached, the feed from the DW process has averaged 90%. At this throughput the E process has been operated in two ways: (1) with 125 cells on final rundown and 25 cells used to reconcentrate weaker cuts from the final rundown cells; and (2) with 150 cells on final rundown and all material below the concentration of feed from DW process returned to DW. Either method is satisfactory, the second being simpler to manipulate.

Voltage drops in excess of 3.5 volts per cell will cause overheating of the cell contents. The voltage drop across each cell may be read at any time during electrolysis on a check panel mounted in the cell room, and those showing excessive drop can be electrically bypassed until the difficulty has been corrected.

Although the entire direct current system in the cell room is isolated from ground, the possibility of an accidental grounding at one end or the other always exists so that the piping and steel equipment must be considered "hot busses" and treated with extreme care due to the high voltages involved. An electrical ground detector is provided to indicate any current leaks to ground and gives audible and visual warning of the condition.

RECOVERY OF ELECTROLYTIC CELL OFF-GAS

The gases evolved during electrolysis (deuterium, hydrogen, and oxygen) are recovered by burning and condensing. The gases leave the cells saturated with water vapor and containing entrained liquid. Some of the entrainment is removed in the vapor-liquid separators located at

the end of each cell row off-gas header. The gases next pass through an ammonia-cooled heat exchanger which condenses and drains off most of the remaining moisture. The gas leaving the ammonia cooler, at about 7°C, is fed to the burner-condensers.

To maintain a stable flame at the burner, the gas velocity through the burner nozzles must be in excess of the propagation rate of a hydrogen-oxygen flame, which is about 21 feet per second. In each burner the gas is passed through a multiport orifice containing 6 holes, each 3/32 inch in diameter. The cell pressure must be between 3 and 4 psig for stable burning with this orifice configuration. Sight glasses, located in the burner heads, allow the operator to observe flame characteristics during burning. A small amount of excess oxygen is added during burner startup, but as burning becomes stable, the flow of excess oxygen is reduced to a rate just sufficient to ensure complete oxidation of the hydrogen isotopes.

The gases are ignited in the burner by two hot wire electrical resistance igniters located adjacent to the orifices. Both igniters are kept on at all times during cell operation to ensure continuity of combustion. Fluctuations in the velocity of the gas through the orifices can cause the burner flame to propagate backward through the orifice resulting in an explosion in the process gas lines and cells. This phenomenon called "flashback," is purposely brought about under controlled conditions to shut down the cell rows. Uncontrolled flashbacks will usually blow liquid seals throughout the system and necessitate re-establishing these seals before continuing the operation. Velocity fluctuations at the burner nozzles are minimized by the prior removal of entrained moisture in the separator and cooler discussed above. Accurate machining of the burner nozzles to ensure uniform orifices free of burrs, and the use of oxygen to smooth out the burner operation when fluctuating gas velocities are expected also aid in eliminating unscheduled flashbacks. It should be noted that the explosive recombination of hydrogen and oxygen results in relatively high pressures inside the process equipment. However this pressure peak is so brief that there is no damage to sensitive equipment, e.g., glass connectors do not break, relief valves do not open, etc. provided the initial system before the flashback is at less than two atmospheres absolute pressure,

The water formed in the burners is condensed and cooled in the lower water-jacketed section of the burners and segregated in "cut" tanks according to its D₂O content.

PRODUCT PURIFICATION

The cell residue containing a minimum of 99.80% D₂O and electrolyte is discharged by gravity to the final residue tank. From there it is pumped to a hold tank from which it flows by gravity into the final evaporator.

The evaporator is operated with its fractionating column on total reflux at 0.1 to 0.4 gallon per minute, with a small side stream fed through a conductivity cell. A purge of nitrogen gas is passed into the kettle and out the condenser vent during this period of operation to carry volatile materials out of the system. When the conductivity of the distillate drops below 15 micromhos/cm, the product is distilled over to the storage tanks. When the conductivity of the product can no longer be held within specifications near the end of the distillation run, the condensate is diverted to a final product cut tank for reworking. The final product concentration in the storage tanks is 0.03 to 0.05% lower than the cell residue due to isotopic dilution occurring in the cell draining and final purification operations.

The electrolyte remaining as residue in the final evaporator is redissolved with burner condensate of approximately cell feed composition. The solution is drained from the kettle and pumped through a filter to an electrolyte hold tank for storage prior to reuse.

FINISHED PRODUCT HANDLING

The finished product is stored in tanks which are vented to the atmosphere through tubes containing a desiccant. The product in each tank is analyzed for adherence to all specifications, filtered, and weighed into clean, dry helium-filled 55-gallon aluminum or stainless steel drums. Samples from each drum are taken for analysis, and the drums are sealed and transferred to the final product storage area pending shipment.

PROCESS LOSSES

A major point of concern in the operation of the process is the loss of deuterium from the system. Process equipment, piping, and the physical layout of the area are designed to keep these losses at an absolute minimum.

All gases vented from tanks are passed through an ammonia cooler or desiccant trap where moisture is collected and returned to the system. All floor drainings are collected in a sump and retained until analyzed. All piping involved in a "flashback" is pressure tested for leaks prior to the resumption of electrolysis.

To keep losses through leaks and accidents at a minimum, all potential sources of leaks are inspected routinely and frequently, and all valve manipulations are rigidly scheduled.

INERT GAS BLANKETING

Originally the cell banks were blanketed with helium gas during filling and draining; however, since 1956, nitrogen gas has been used for this purpose. Analyses of burner condensate have shown no increase in the concentration of oxides of nitrogen over that present during the period

that helium had been used. A continuous nitrogen gas purge of the final product evaporator during the reflux and distillation operations removes traces of ammonia which is formed during electrolysis through the reduction of nitrogen oxides present in the burner condensate.

EQUIPMENT DESCRIPTION

The equipment used in the E process comprises, except for the cells and burners, simple standard pieces such as are found in any batch chemical operation carried out on a small scale. The major equipment pieces are listed below.

FEED PURIFICATION AND FINAL PRODUCT STILLS

These stills are vertical, 450-gallon steam-jacketed kettles with agitators, open-tube fractionating columns and condensers. The jacket can be heated with steam or cooled with water. Rotameters are provided to indicate rate of flow of distillate to the receiver and reflux to the column.

ELECTROLYTIC CELLS

The electrolysis is done in 150 vertical cylindrical cells having water-cooled inner and outer carbon steel cathodes and concentric nickel anodes. See Figure 30 for their dimensions and general arrangement. Their charge capacity is about 140 lb per cell, and the normal operating current is 1000 amperes. All cells are operated electrically in series, but are banked in six parallel rows of 25 cells. The rows operate independently with regard to liquid and gas flows. The cells are insulated from connecting piping with "Tygon" or glass connectors.

CELL OFF-GAS SEPARATORS

Six liquid-gas separators, one at the end of each cell gas header on each row of cells, have been provided to collect any entrained electrolyte solution.

GAS COOLERS AND SEPARATORS

Ammonia-refrigerated, vertical, coil-in-jacket coolers are used to condense and remove water vapor from cell gases prior to burning.

BURNER-CONDENSERS

The burners are vertical, water-jacketed cylindrical chambers in the tops of which the cell gases are recombined by burning. The water vapor formed is condensed on the jacket walls. Each burner is provided with two multiport burner nozzles and two hot-wire igniters.

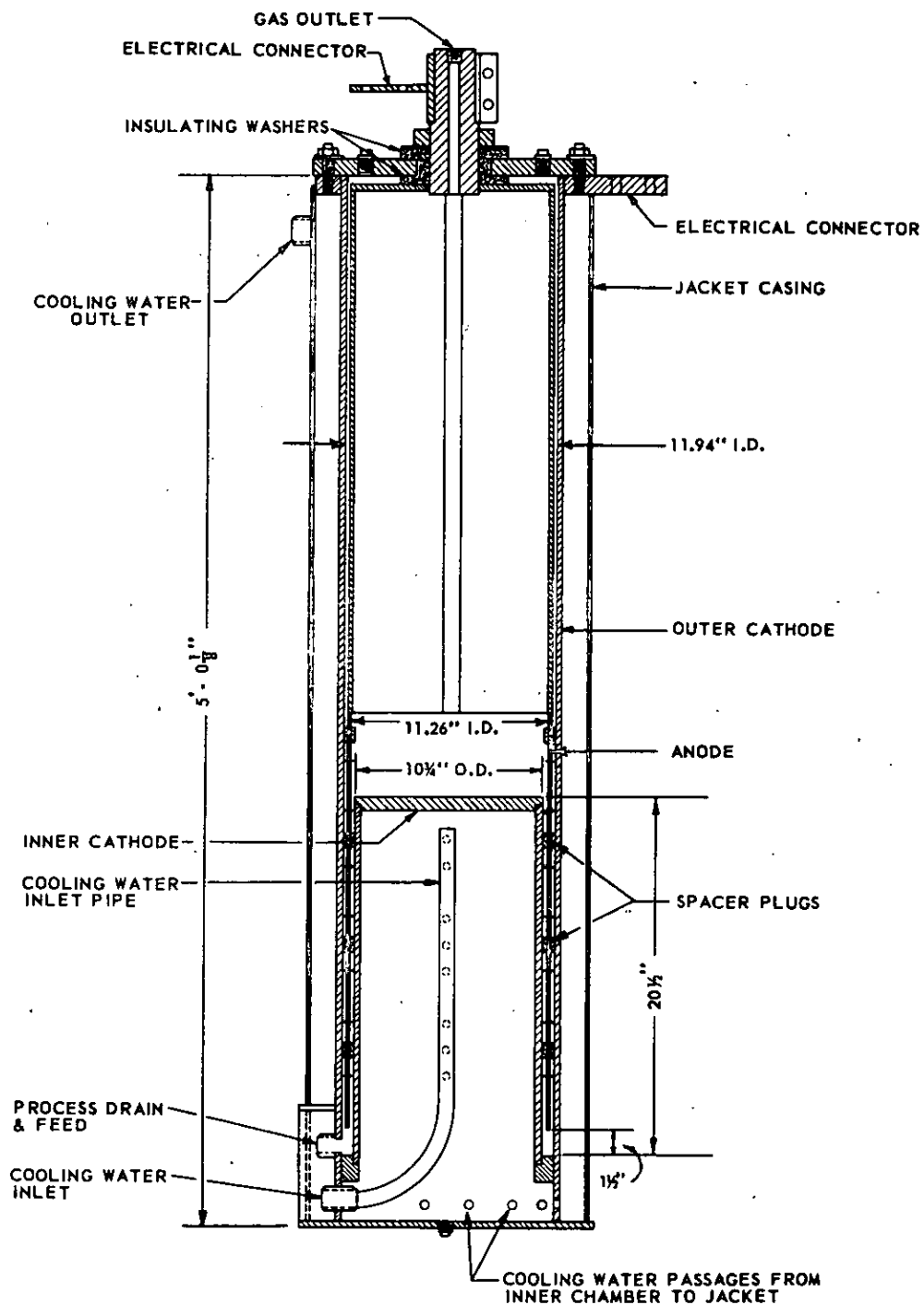


FIGURE 30 - E PROCESS ELECTROLYTIC CELL

The nozzles are used singly. Figure 31 shows the general configuration of the burner. The burner chamber is stainless steel and the jacket is carbon steel.

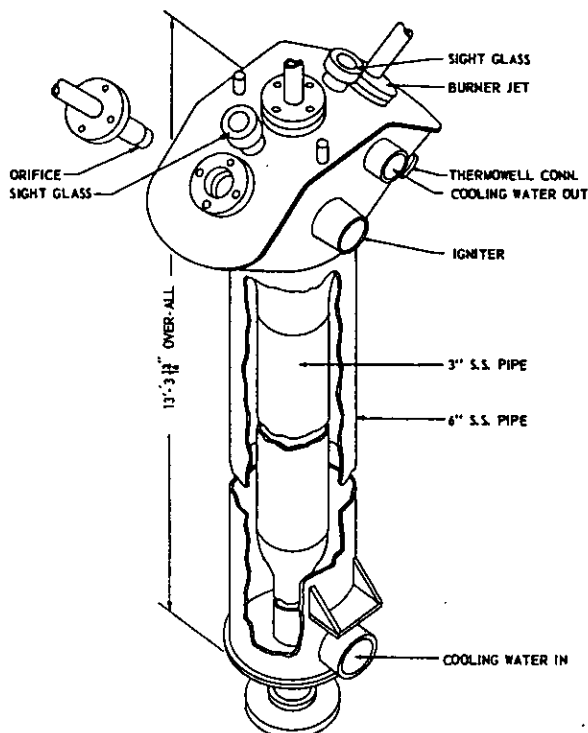


FIGURE 31 - E PROCESS BURNER-CONDENSER

PUMPS

All process pumps are vertical centrifugal pumps having a capacity of 25 gpm at a 50 ft discharge head. The pump casing and shaft are extended so that the shaft seal is above the liquid level of the supply tank from which the pump draws its feed.

TANKS

All storage, feed, residue and hold tanks in the process are cylindrical carbon steel tanks except those which contain electrolyte-free burner condensate (the cut tanks), and those containing distilled final product.

AUXILIARY EQUIPMENT

RECTIFIER AND SWITCHGEAR

Two rectifier units are used (one as a spare) to supply direct current to the cells. The main rectifier is a Westinghouse "Unit Substation"

that is designed to supply 1000 amperes DC at a maximum of 525 volts. The equipment includes 6 water-cooled "Ignitron" tubes with necessary circuit breakers, transformers, voltage controls, and heat removal facilities.

The spare rectifier is capable of operating two cell rows. This is a General Electric unit having a capacity of 1000 amperes at a maximum of 160 volts. It is also an Ignitron rectifier essentially similar to the large Westinghouse unit.

AMMONIA REFRIGERATION EQUIPMENT

One-ton and four-ton ammonia compression refrigeration units, with condensers and receivers, are provided to cool cell gases prior to burning, and to refrigerate tank vent gases to prevent material losses.

PROCESS CONTROL

STANDARD E PROCESS CONDITIONS

A listing of the standard E process conditions is given below in Table XXIII, including product and raw material quality specifications.

TABLE XXIII

Standard E Process Conditions

Final Product Specifications

D ₂ O content (mol %)	99.75%
Conductivity	15 micromhos/cm max.
Permanganate demand	1 x 10 ⁻⁵ mg/ml D ₂ O max.
Color	APHA Standard No. 5 max.
Turbidity	Clear

Raw Material Specifications

Potassium carbonate (anhydrous)	
H ₂ CO ₃ content	99+%
Potassium permanganate	
KMnO ₄ content	99+%
Oxygen (water pumped)	
Oxygen content	99+%
Nitrogen (water pumped)	
Nitrogen content	99+%

Process Control Conditions

Cell Operation

Voltage drop across cell	3.5 volts max.
G. E. rectifier system	
Amperage	1,000 amp max.
Voltage	160 volts max.
Westinghouse rectifier system	
Amperage	1,000 amp max.
Voltage	575 volts max.
Cooling water rate	2 - 3 gpm min.
Cell cooling water exit temperature	16 - 20°C
Current density	0.42 - 0.84 amp/in ²
Electrolyte concentration in cell charge	6 - 8 wt %

Process Gas Recovery System

Temperature of gases from cells	20 - 25°C
Temperature of process gas from ammonia coolers	7 - 10°C
Gas pressure at burners	3 - 4 psig
Temperature of cooling water from burners	50°C max.
Temperature of liquid ammonia to coolers	7°C min.
Process gas pressure at cell header	3 - 4 psig
Internal burner pressure	0 - 3.0 in. H ₂ O

Final Evaporator Operation

Boilup rate at total reflux	0.10 - 0.40 gpm
Rate of drawoff to heads tank	0.10 - 0.40 gpm
Rate of finished product drawoff	0.10 - 0.40 gpm
Cooling water temperature to condenser and after-cooler	15 - 20°C
Product temperature from final condenser	95°C max.
Product temperature from after-cooler	20 - 25°C

Permanganate Treating

Permanganate demand after treatment treatment	None (excess MnO_4^- in kettle)
Temperature of distillate from condenser	50°C max.
Boilup rate at total reflux	0.10 - 0.40 gpm
Rate of distillate drawoff	0.10 - 0.40 gpm
Time at total reflux	60 - 90 minutes
Condenser cooling water inlet temperature	15 - 20°C

SCHEDULING AND CONTROL OF CELL OPERATION

Because of the flexibility of the E process and the range of cell feed concentrations that are encountered, a rigid operating program cannot be set up far in advance. Certain guiding principles can, however, be stated, and typical examples of the calculations necessary will illustrate the application of these principles and suggest variations that may prove desirable. These principles include:

1. The percentage of a cell charge that must be electrolyzed to obtain a desired concentration of residue depends on the concentration of the charge and on the actual separation factor achieved in the plant cells. From operating experience this factor is between 8.0 and 10.0, but may be expected to vary somewhat. Actual values of the separation factor were calculated from plant operating data (See Appendix F).

2. All runs should be calculated to leave more than 3.5 gallons in each cell at completion of a run. If less than this quantity remains, flashbacks may damage the nickel anode.

3. The inventory of heavy water in the plant is determined largely by the schedule set up for handling the "cuts" of burner condensate from the cells. Inventory in process will be low if a large number of cuts of graded concentration are taken and if these are charged to the cells whenever the cell concentration matches that of a cut tank. This procedure, however, calls for many interruptions to electrolysis with attendant troubles with flashbacks, burner adjustments and the like.

Difficulties in manipulation are minimized if cuts are few in number and if they are accumulated until there is enough of a given cut to make a full charge to an operable bank of cells. This procedure, however, increases the holdup of D_2O in process.

In practice, cuts are scheduled according to conditions desired in the plant. The condensate formed during the last 24 hours of electrolysis of each final product run is accumulated for dissolving the potassium carbonate left in the final evaporator after distilling. A condensate cut of concentration equal to that of normal feed is combined with incoming feed material from the DW plant. When operating five cell rows with DW process feed, enough of the lower concentration burner condensate cuts are saved to operate one row. All remaining material is returned to DW.

If desired all cells may be operated on final product, in which case all material below the concentration of the feed from the DW process is recycled to DW.

If the separation factor and the D_2O content of the burner condensate are known, the D_2O content of the cell residue can be calculated (See Appendix F). If the desired product concentration is 99.75% D_2O , and the separation factor is 8, then the electrolysis must be continued until the overhead concentration is at least 98.0%. In practice, the overhead concentration is carried to 99.0% to allow for dilution of the cell residue in the subsequent operations involving transfer, distillation, storage, and packaging. This dilution may occur whenever the concentrated material is exposed to air or other gas containing the vapor of natural water.

PERSONNEL SAFETY

The principal hazards of the E process are those attendant to the use of direct current at up to 600 volts through uninsulated conductors, and the handling and burning of explosive mixtures of hydrogen with oxygen. There are also chemical burn hazards involved with the handling of potassium carbonate and potassium permanganate.

Any personnel entering the cell room when the cells are in operation are required to wear electrically tested rubber gloves, rubber overshoes, and goggles. The process lines and cells in the cell room are regarded as electrically "hot", although the entire DC circuit is isolated from ground. As an additional safeguard, equipment is provided to give audible and visual warning of electrical grounds.

The cells, burners, and interconnecting piping have been designed to withstand explosion of the H_2-O_2 mixtures within them. The sight glasses in the cell gas lines and the glass bubble bottles at the burners are provided with transparent plastic shields to stop flying fragments if they are shattered by the force of a "flashback."

Rubber gloves, coveralls, and rubber goggles are worn when working with potassium carbonate and permanganate, and deluge showers are located in the work areas where these chemicals are handled.

ANALYTICAL CONTROL

The E process is a series of batch operations, each controlled on the basis of analysis of the process material at the beginning and end of each batch. Between operations the process liquid is stored in tanks. The analysis of the material in these tanks must be known for process planning, and periodically all material in process must be analyzed for inventory control. An average of 6 control samples must be analyzed per day and about 30 samples for monthly inventory (for the analytical methods used see Appendix D). The control analyses required are as follows:

- (1) Each incoming batch of feed from the DW process is analyzed for D_2O content.
- (2) The treated feed and electrolyte mix are analyzed for D_2O content and for electrolyte concentration before charging to the cells.
- (3) The burner condensate is analyzed for D_2O content periodically during the cell run. This analysis indicates the D_2O content of the cell residue, and determines the end point of the electrolysis operation.
- (4) The contents of each drum are analyzed for all specifications prior to sealing and storing.

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APPENDIX A

EQUILIBRIUM CONCENTRATIONS OF H_2O , HDO , AND D_2O IN WATER

The concentration of heavy water as used in the text of this manual means the molar ratio $\text{D}/(\text{D} + \text{H}) \times 100$. This is the same numerically as $\text{D}_2\text{O}/(\text{D}_2\text{O} + \text{H}_2\text{O}) \times 100$ and is half the value $\text{HD}/(\text{HD} + \text{H}_2) \times 100$, or $\text{HDO}/(\text{HDO} + \text{H}_2\text{O}) \times 100$.

In the feed water, which contains only one atom of D per 7000 atoms of H, the D is present as HDO. At high concentrations of heavy water, the predominate species is D_2O with H present as HDO. The three molecular species are related by the equation,



The equilibrium constant for this reaction is

$$K = \frac{[\text{HDO}]^2}{[\text{H}_2\text{O}][\text{D}_2\text{O}]} \quad (\text{A-2})$$

This constant, and therefore the relative proportions of the three molecules, varies somewhat with temperature ($K = 3.26$ at 25°C and 3.40 at 100°C). The concentrations of each of the species for any given over-all concentration of deuterium [D] can be calculated readily from equation (A-2) with the aid of two further relations,

$$[\text{D}_2\text{O}] + [\text{HDO}] + [\text{H}_2\text{O}] = 1.0 \quad (\text{A-3})$$

$$[\text{D}] = [\text{D}_2\text{O}] + \frac{[\text{HDO}]}{2} \quad (\text{A-4})$$

The concentrations of the three molecules that are actually present in heavy water of various concentrations are given in Figure A-1.

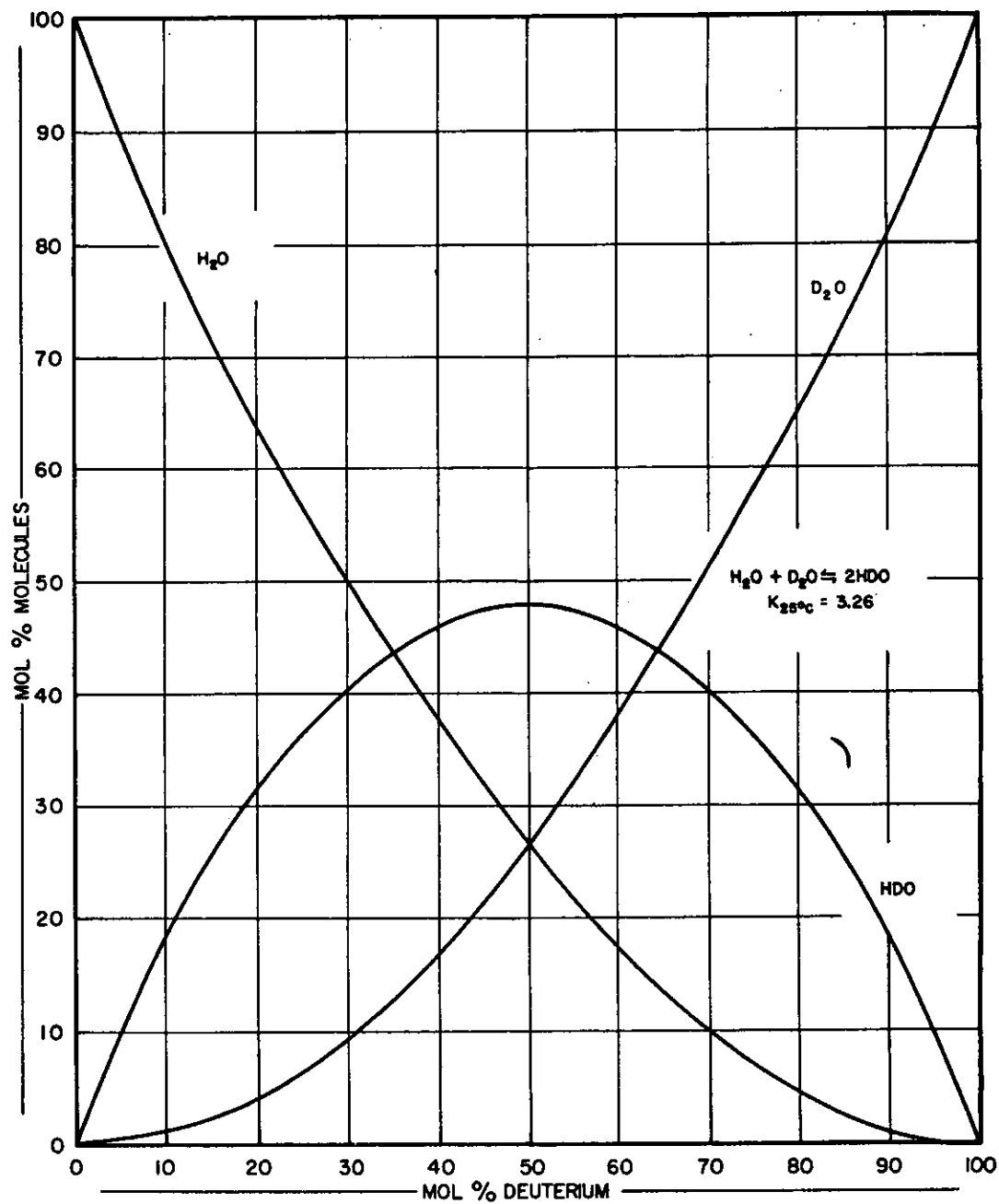


FIGURE A-1 - EQUILIBRIUM CONCENTRATIONS OF H₂O, HDO, AND D₂O vs. OVER-ALL CONCENTRATION OF DEUTERIUM IN WATER

APPENDIX B

SAMPLE CALCULATION - DANA - FIRST STAGE

DESIGN BASIS

Cold tower temperature	30°C (86°F)
Hot tower temperature	120°C (248°F)
Cold tower pressure	
bottom	254 psia
top	245
average	250
Hot tower pressure	
bottom	272 psia
top	263
average	268

ALLOWABLE GAS RATE - HOT TOWER

Vapor pressure of H₂O at 248°F - 28.8 psia
 Specific volume of saturated H₂O vapor at 248°F - 14.282 ft³/lb
 Ideal specific volume at 248°F and 28.8 psia

$$\frac{359}{18.0} \times \frac{14.7}{28.8} \times \frac{708}{492} = 14.63 \text{ ft}^3/\text{lb}$$

Compressibility of H₂O vapor

$$Z_{\text{H}_2\text{O}} = \frac{14.282}{14.63} = 0.9760$$

Compressibility of H₂S (see Figure B-3, page 139)

Pressure	$Z_{\text{H}_2\text{S}}$	
	220°F	280°F
220	0.9480	0.9612
300	0.9210	0.9415

Partial pressure of H₂S at top of hot tower

$$263 - 28.8 = 234.2 \text{ psia}$$

By interpolation, at 234.2 psia and 248°F,

$$Z_{\text{H}_2\text{S}} = 0.9461$$

Mol ratio humidity (see Figure B-1, page 138)

$$H_{\text{th}} = \frac{28.8}{234.2} \times \frac{0.9461}{0.9760} = 0.1192$$

Molar densities

$$\frac{1.0 \times 263}{0.9461 \times 10.72 \times 708} = 0.03662 \text{ mols H}_2\text{S/ft}^3$$

$$\frac{1.0 \times 263}{0.9760 \times 10.72 \times 708} = 0.03550 \text{ mols H}_2\text{O/ft}^3$$

(10.72 = Gas law constant)

Partial density - H₂S

$$\frac{1}{1.1192} \times 0.03662 \times 34.08 = 1.115 \text{ lb/ft}^3$$

Partial density - H₂O

$$\frac{0.1192}{1.1192} \times 0.0355 \times 18.02 = 0.068 \text{ lb/ft}^3$$

Density of mixture 1.183 lb/ft³

Allowable vapor velocity

Tray spacing - 18 in.

Liquid seal - 1-1/2 in.

K_v - 0.13 in.

Vapor velocity = 0.907 ft/sec

F factor

$$\begin{aligned} F &= v \sqrt{\rho} \\ &= 0.907 \sqrt{1.183} \\ &= 0.988 \end{aligned}$$

Allowable total first stage hot tower gas rate

Tower area

Four 12 ft ID towers - 452 ft²

Vapor rate

$$0.907 \times 452 = 410 \text{ ft}^3/\text{sec}$$

Molar volume of components

$$\text{H}_2\text{S} = \frac{1}{0.03662} = 27.3 \text{ ft}^3/\text{lb mol}$$

$$H_2O = \frac{1}{0.0355} = 28.2 \text{ ft}^3/\text{lb mol}$$

Mol volume of mixture

$$\frac{27.3 \times 1.0 + 0.1192 \times 28.2}{1.1192} = 27.4 \text{ ft}^3/\text{lb mol}$$

Total molar gas flow - hot towers

$$\frac{410 \times 3600}{27.4} = \underline{53,870} \text{ mols/hr}$$

$$H_2S - 48,130$$

$$H_2O - \underline{5,740}$$

$$\text{Total } 53,870$$

CALCULATION OF β

$$\beta = \frac{(1+H) (S+K_x)}{\alpha(1+S) (1+HK_x)}$$

$$K_x = 1.010 e^{233/T}$$

$$\alpha = 1.1596 e^{-65.43/T}$$

Cold Tower Conditions

$$\text{Average pressure} - 249.5 \text{ psia}$$

$$\text{Temperature} \quad 30^\circ\text{C} (186^\circ\text{F})$$

$$303^\circ\text{K}$$

$$K_x = 1.010 e^{233/303}$$

$$= \underline{2.1792}$$

$$\alpha = 1.1596 e^{-65.43/303}$$

$$= \underline{0.9343}$$

$$H_c = \underline{0.00215} \text{ (by methods directly parallel to those for calculation of } H_{th})$$

Solubility of H_2S in H_2O - S_c

Solubility at 30°C and 248.9 psia partial pressure
1.40 mols/liter (Figure B-2, page 139)

$$1.40 \times 34.08 = 47.71 \text{ gm H}_2\text{S/liter}$$

$$1000 - 47.71 = 952.29 \text{ gm H}_2\text{O/liter}$$

$$\frac{952.29}{18.02} = 52.85 \text{ mols H}_2\text{O/liter}$$

$$S_c = \frac{1.40}{52.85} = 0.0265 \text{ mols H}_2\text{S/mol H}_2\text{O}$$

$$\beta_c = \frac{(1 + 0.00215)(0.0265 + 2.1792)}{(0.9343)(1 + 0.0265)(1 + 0.00215 \times 2.1792)}$$

$$\beta_c = 2.2941$$

$$m_c = \frac{1}{\beta_c} = 0.4359$$

By parallel methods of calculation

For the hot tower

Temperature - 120°C (248°F)
393°K

Pressure (avg.) - 267.5 psia

$$H_h = 0.1168$$

$$S_h = 0.00763$$

$$\beta_h = 1.7074$$

$$m_h = \frac{1}{\beta_h} = 0.5857$$

OPTIMUM LIQUID AND GAS FLOWS

Equations

$$L_c \left(\frac{S_c}{1 + S_c} \right) + G_h \left(\frac{1}{1 + H_h} \right) = L_h \left(\frac{S_h}{1 + S_h} \right) + G_c \left(\frac{1}{1 + H_c} \right) \quad (12)$$

$$L_c \left(\frac{1}{1 + S_c} \right) + G_h \left(\frac{H_h}{1 + H_h} \right) = L_h \left(\frac{1}{1 + S_h} \right) + G_c \left(\frac{H_c}{1 + H_c} \right) + L_p \quad (13)$$

$$\frac{L_c}{G_c} \cdot \frac{1}{\beta_c} = \frac{1}{\beta_h} \cdot \frac{L_h}{G_h} \quad (27)$$

$$\begin{array}{lll}
S_c = 0.0265 & \frac{1}{1 + S_c} = 0.97418 & \frac{S_c}{1 + S_c} = 0.02582 \\
S_h = 0.00763 & \frac{1}{1 + S_h} = 0.99243 & \frac{S_h}{1 + S_h} = 0.00757 \\
H_c = 0.00215 & \frac{1}{1 + H_c} = 0.99785 & \frac{H_c}{1 + H_c} = 0.00215 \\
H_h = 0.1168 & \frac{1}{1 + H_h} = 0.89542 & \frac{H_h}{1 + H_h} = 0.10459
\end{array}$$

Let $L_c = 1.000$

Assume $\frac{L_c}{G_c} = 0.4809$

(This value, used for illustration, represents the final trial in a solution by successive approximations)

$$G_c = \frac{1.000}{0.4809} = 2.0794$$

Using equation (27)

$$\frac{0.4809}{0.4359} = \frac{0.5857}{L_h/G_h}$$

$$\frac{L_h}{G_h} = \frac{0.5857 \times 0.4359}{0.4809}$$

$$L_h = 0.5309 G_h$$

Using equation (12)

$$1.000 \times 0.02582 + 0.89542 G_h = 0.5309 \times 0.00757 G_h + 2.0794 \times 0.099785$$

$$G_h = \frac{2.04911}{0.89140}$$

$$= 2.2988$$

$$L_h = 0.5309 \times 2.2988$$

$$= 1.2204$$

Check in equation (13)

(L_p is negligible in 1st stage)

$$1.000 \times 0.97418 + 2.2988 \times 0.10459 \approx \\ 1.2204 \times 0.99243 + 2.0794 \times 0.00215$$

$$1.21461 \approx 1.2156$$

(Checks within 1 part in 1000, sufficiently close for these calculations)

Total first stage flows from above relative flows and allowable G_h

$$L_c = 53,870 \times \frac{1.000}{2.2988} = \underline{23,400} \text{ mols/hr}$$

$$G_c = 23,400 \times 2.0794 = \underline{48,700}$$

$$L_h = 23,400 \times 1.2204 = \underline{28,600}$$

$$G_h = \underline{53,870}$$

(These are very close to the design figures before application of the 10% for safety factor.)

$$\begin{aligned} \text{Feed} - L_o &= \frac{L_c}{1 + S_c} \\ &= 23,400 \times 0.97418 = \underline{22,800} \text{ mols/hr} \end{aligned}$$

Gas to Blowers

$$\begin{aligned} G_o &= G_c + L_o - L_c \\ &= 48,700 + 22,800 - 23,400 \\ &= \underline{48,100} \text{ mols/hr} \end{aligned}$$

GAS AND LIQUID COMPOSITIONS AT TOP OF COLD AND BOTTOM OF HOT TOWERS

Top of Cold Tower
Equation (29)

$$y_{tc} = \frac{x_{tc}}{0.98\beta_c}$$

x_{tc} is less than x_f because of solution of 600 mols H_2S in 22,800 mols feed.

$$x_{tc} = \frac{22,800 \times 0.000147 + 600 y_{tc}}{23,400}$$

$$y_{tc} = \frac{x_{tc}}{0.98 \times 2.294} = 0.4448 x_{tc}$$

$$x_{tc} = \frac{22,800 \times 0.000147 + 600 \times 0.4448 x_{tc}}{23,400}$$

$$23,400 x_{tc} - 267 x_{tc} = 3.3516$$

$$x_{tc} = \frac{3.3516}{23,133} = 0.000145$$

$$y_{tc} = 0.4448 \times 0.000145 \\ = 0.0000644$$

Bottom of Hot Tower

Equation (35)

$$G_h y_{bh} = G_o y_{tc} + G_s \left(\frac{x_{bh}}{K_{xh}} \right) + G_w x_{bh}$$

Equation (30)

$$y_{bh} = \frac{0.98 x_{bh}}{\beta_h}$$

$$= \frac{0.98 x_{bh}}{1.7074}$$

$$= 0.5740 x_{bh}$$

$$G_h = 53,870$$

$$G_o = 48,100$$

$$G_s = L_h \left(\frac{S_h}{1 + S_h} \right)$$

$$= 28,600 \times 0.00757$$

$$= \underline{216.5}$$

$$G_w = G_h - G_o - G_s$$

$$= 53,870 - 48,100 - 216$$

$$= \underline{5554}$$

$$K_{xh} = 1.8275$$

$$53,870 \times 0.5740 x_{bh} = 48,100 \times 0.0000644 + 216 \left(\frac{x_{bh}}{1.8275} \right) + 5554 x_{bh}$$

$$30921 x_{bh} - 118 x_{bh} 5554 x_{bh} = 3.09764$$

$$x_{bh} = \frac{3.09764}{25249}$$

$$= \underline{0.0001226}$$

$$y_{bh} = 0.5740 \times 0.0001226$$

$$= \underline{0.0000704}$$

NUMBER OF THEORETICAL PLATES - COLD TOWER

Equation (36)

$$N_p = \frac{\log [(1-P)M + P]}{\log 1/P}$$

Equation (37)

$$P_c = \frac{m_c}{R_c}$$

Equation (39)

$$M_c = \frac{y_{bc} - m_c x_{tc}}{y_{tc} - m_c x_{tc}}$$

The requirement is that x_{bc} be about four times the feed composition.

Let x_{bc} , then = 0.00060

$$R_c = \frac{y_{bc} - y_{tc}}{x_{bc} - x_{tc}}$$

Since R_c = slope of operating line

$$0.4809(0.00060 - 0.000145) = y_{bc} - 0.0000644$$

$$y_{bc} = \underline{0.0002832}$$

$$M_c = \frac{0.0002832 - 0.4359 \times 0.000145}{0.0000644 - 0.4359 \times 0.000145}$$

$$= \frac{0.0002198}{0.000001194}$$

$$= \underline{184}$$

$$P_c = \frac{0.4359}{0.4809} = \underline{0.9064}$$

$$N_p = \frac{\log [(1 - 0.9064) 184 + 0.9064]}{\log \frac{1}{0.9064}}$$

$$= \frac{\log 18.124}{\log 1.1032}$$

$$= \underline{29.5} \text{ theoretical plates}$$

RECOVERY

x - intercepts of operating lines

$$x_{c_o} = x_{tc} - \frac{y_{tc}}{0.4809}$$

$$x_{h_o} = x_{bh} - \frac{y_{bh}}{0.5309}$$

$$x_{c_o} = 0.000145 - \frac{0.0000644}{0.4809}$$

$$= \underline{0.000011}$$

$$x_{h_o} = 0.0001226 - \frac{0.0000704}{0.5309}$$

$$= \underline{-0.000010}$$

Equation (25)

$$\text{Recovery} = x_p L_p = L_c x_{c_o} - L_h x_{h_o}$$

$$= 23,400 \times 0.000011 - 28,600 (-0.000010)$$

$$\begin{aligned}
 &= 0.257 + 0.286 \\
 &= \underline{0.543} \text{ mols/hr}
 \end{aligned}$$

CALCULATION AIDS

The following figures present in convenient form several of the intermediate quantities calculated from the fundamental physical data.

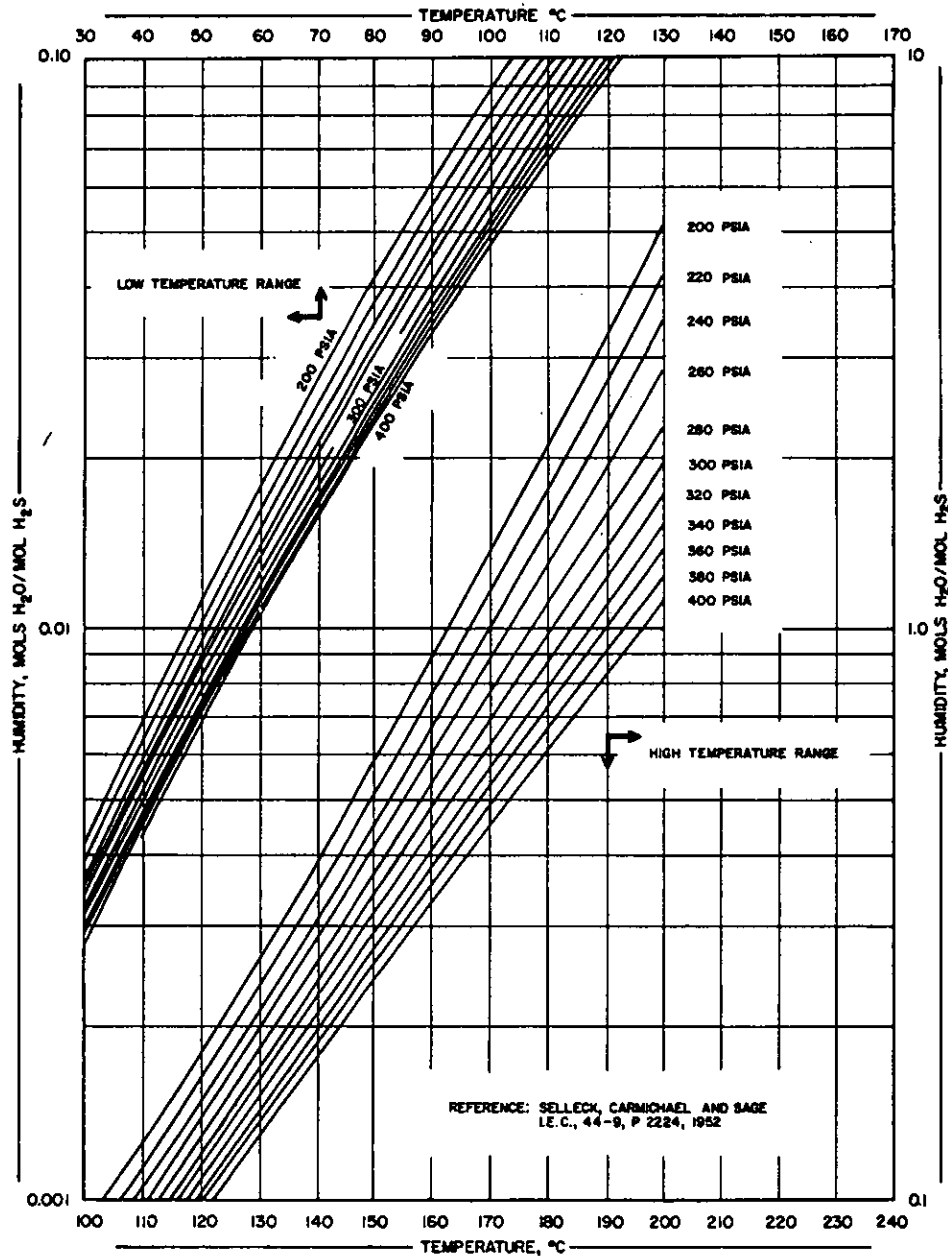


FIGURE B-1 - HUMIDITY OF H₂O(V) IN H₂S(G)

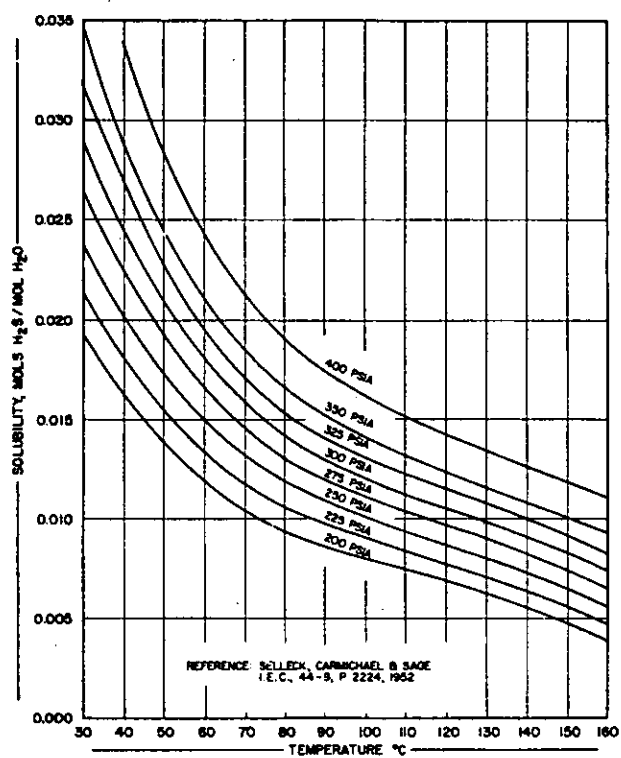


FIGURE B-2 - SOLUBILITY OF $H_2S(G)$ IN $H_2O(L)$

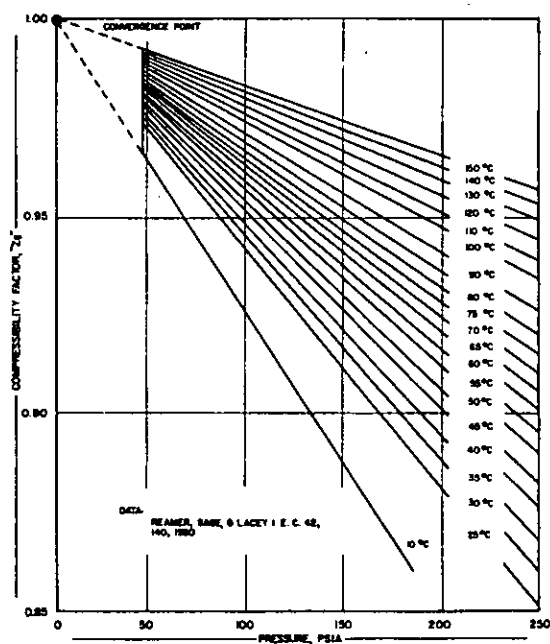


FIGURE B-3 - COMPRESSIBILITY OF H_2S GAS

APPENDIX C

GLOSSARY OF TERMS USED IN GS PROCESS CALCULATIONS

A gain in concentration of D_2O (value of x) over n theoretical plates in GS tower, expressed as mol fraction

a gain in concentration of D_2O (value of x) across first theoretical plate of GS tower (by first plate is meant the first step on McCabe-Thiele diagram, i.e., top of cold or bottom of hot tower), expressed as mol fraction

b (subscript) - indicates condition at bottom of tower

c (subscript) - indicates condition in cold tower

F correlation factor for allowable gas velocity through tower

$$F = v \sqrt{\rho}$$

upper limit of value of F for good design, and the value used in determining allowable throughput and therefore capacity of GS unit is 1.0

f (subscript) - denotes feed condition

G total flow, gas phase, mols per hour - includes H_2S gas plus associated water vapor (unless otherwise noted) without regard for isotopic composition

G_o gas flow to first stage blower, H_2O free

G_c average gas flow in cold tower

G_h average gas flow in hot tower

G_s gas stripped from waste (does not include water vapor)

G_w water vapor added to gas stream in humidifier, from stripper, and as direct steam to bottom of hot tower (does not include H_2S)

H humidity, expressed as mol ratio of water vapor to dry gas, without regard to isotopic content, calculated as follows:

$$H = \frac{(p_{H_2O}) (z_{H_2S})}{(p_{H_2S}) (z_{H_2O})}$$

- P_{H_2O} vapor pressure of water at temperature chosen
- P_{H_2S} partial pressure of H_2S , equal to total pressure of less P_{H_2O}
- Z_{H_2S} compressibility of $H_2S^{(10)}$ at P_{H_2S} and temperature chosen
- Z_{H_2O} compressibility of H_2O vapor, calculated by dividing specific volume of saturated vapor at temperature chosen by the ideal gas law specific volume calculated at temperature chosen and P_{H_2O}

H_c average humidity in cold tower

H_h average humidity in hot tower

h (subscript) - indicates condition in hot tower

K_x equilibrium constant for the liquid phase reaction:



$$K_x = \frac{[HDO]_l [H_2S]_l}{[HDS]_l [H_2O]_l}$$

Where the formula in brackets with subscript l denotes molar concentration in liquid phase expressed as mols per liter.

$$K_x = 1.010 e^{-233/T} \quad (5)$$

K_{xc} constant at cold tower temperature

K_{xh} constant at hot tower temperature

L total flow, liquid phase, mols per hour - includes water plus dissolved H_2S (unless otherwise noted) without regard for isotopic content

L_o feed to first stage, H_2S free

L_c average liquid flow in cold tower

L_h average liquid flow in hot tower

L_p product withdrawal rate, H_2S free

M enrichment ratio used in Colburn method for calculating N_p , the number of theoretical plates in a tower (See equation (36), (39), and (40), pages 51 and 52)

M_c enrichment ratio in cold tower

M_h enrichment ratio in hot tower

m slope of equilibrium line, in dilute region (up to 1.0 mol per cent) $m = 1/\beta$

m_c slope of cold tower line

m_h slope of hot tower line

m (subscript) - denotes condition at mid-point (middle theoretical plate) of column

N_p number of theoretical plates required for a given separation, used in Colburn method, see equation (36), page 51

n plate number

P ratio of slopes of operating and equilibrium lines as used in Colburn method for determining N_p , P is always less than 1.0.

$$P_c = \frac{m_c}{R_c} \quad \text{in cold tower}$$

$$P_h = \frac{R_h}{m_h} \quad \text{in hot tower}$$

p (subscript) - refers to product

Q reciprocal of P - always greater than 1.0

R slope of operating line of McCabe-Thiele diagram, the ratio L/G

$$R_c = \frac{L_c}{G_c} \quad \text{in cold tower}$$

$$R_h = \frac{L_h}{G_h} \quad \text{in hot tower}$$

r distance between x-intercepts of cold and hot tower operating lines on McCabe-Thiele plot

S solubility, expressed as mol ratio of H_2S to water in liquid phase without regard to isotopic content

S is calculated from solubility data in Figure 17⁽¹⁵⁾, page 52. The calculation of mol ratio is made assuming that the density of the solution is 1000 gm per liter.

S_c average solubility in cold tower

S_h average solubility in hot tower

T temperature, absolute, degrees K

t (subscript) - denotes condition at top of column

v average vapor velocity in tower, ft/sec actual conditions

x molar concentration of deuterium, over-all in liquid phase, includes deuterium in form of HDO and D_2O as well as dissolved HDS and D_2S . Generally used with subscripts, e.g.,

x_{bc} concentration in liquid at bottom of cold tower

x_c concentration in liquid on an indefinite plate in cold tower

x_{c_o} x-intercept of cold tower operating line

x_f concentration in feed water

x_{h_o} x-intercept of hot tower operating line

x_p concentration in product

x_w concentration in waste

For others, see meanings of subscripts in this Glossary.

Y molar concentration of deuterium, over-all, in gas phase. Analogous to x and includes deuterium in all molecular forms. Usually appears with subscripts, e.g.,

y_{bh} concentration in gas phase at bottom of hot tower

- y_s concentration in H_2S from stripper
- Z compressibility of gas or vapor, ratio of actual to ideal specific volume. See definition of H.
- α relative volatility of HDO with respect to H_2O , also assumed to equal relative volatility of HDS with respect to H_2S
- $\alpha = 1.1596 e^{-65.43/T(^{\circ}S)}$
- β over-all distribution coefficient for deuterium in the system

$$\beta = \frac{x(1-y)}{y(1-x)}$$

At concentrations below 1.0 mol %

$\beta \frac{x}{y}$ within the limits of precision of the data

For calculation of β from K_x see equation (8), page 23

ρ gas density, lb/ft^3

I intersection of operating and equilibrium lines

APPENDIX D

WATER TREATMENT PROCESSES

Water, as it occurs in nature, contains impurities either in solution or as suspended solids. The nature and extent of these impurities depend upon the source of water (rain, surface, or ground) and the location of the supply. The most common impurities are calcium and magnesium salts (hardness), dissolved gases, silica, iron, manganese, and organic matter. The water required for the GS process must be neither scale forming, nor corrosive, nor cause a buildup of inert gas within the units; i.e., a water of low hardness with a neutral or slightly alkaline pH, containing a minimum of dissolved gases and suspended solids.

WATER QUALITY

At the Savannah River Plant the source of water for the GS process is the Savannah River, which is composed primarily of the surface runoff from a large area of sand and clay soils. This water is very soft containing only 6 to 10 ppm of hardness (expressed as calcium carbonate). It does contain, however, some dissolved silica and iron, considerable suspended particulate matter (primarily silica and clay suspensions), and an appreciable alkaline carbonate concentration.

The water at the Dana Plant is supplied from Ranney wells located on the bank of the Wabash River. The water obtained from these wells has been naturally filtered, resulting in a very low suspended matter content. It does contain however, a very high calcium and magnesium hardness (300 to 350 ppm as calcium carbonate), and small concentrations of dissolved silica and iron. The hardness is present as dissolved salts which, in the relative order of their abundance are: bicarbonates, sulfates, and chlorides.

SUSPENDED SOLIDS

At the Savannah River Plant the suspended solids, which average about 35 ppm in the river water and are at times as high as 125 ppm, are removed by lime-alum coagulation and precipitation followed by filtration. This treatment reduces the suspended matter concentration to less than 1 ppm during periods of stable operation. It has been found that any increase in turbidity of the GS process feedwater caused by precipitator upset or by abnormally high river water turbidity will promote foaming and carry-over in the first-stage cold towers, which in turn necessitates a reduction in column throughput until control can be re-established.

At the Dana Plant the water is naturally filtered through a 20 to 50-foot bed of sand before entering the laterals of the Ranney wells. This filtering is quite sufficient to maintain the turbidity below 1 ppm. The feed to the GS units is effectively filtered a second time in passing through ion exchange beds.

CALCIUM AND MAGNESIUM HARDNESS

The hardness level of the Savannah River Plant water is so low that no facilities are required for hardness removal; however at the Dana Plant a 10,000,000-gallon per day, completely automatic water-softening facility was constructed to treat all of the GS process feed water. This plant employs an ion exchange softening system in which the calcium and magnesium cations are exchanged for hydrogen and sodium ions. Approximately three quarters of the water passes through the hydrogen exchange units forming a mixed solution of carbon dioxide, sulfuric, and hydrochloric acids. The remaining one quarter passes through the sodium exchange unit forming the respective sodium salts of these acids. The two streams are then blended in a proportion which results in pH of 4.3 whereby all bicarbonates present are converted to carbon dioxide. The effluent from this facility contains less than 5 ppm hardness expressed as calcium carbonate.

The process cooling water at Dana Plant is not softened, and the high hardness of this cooling water requires that an upper limit of 60°C be maintained on all effluent cooling water streams to prevent precipitation of calcium carbonate. In addition to this temperature limit, 5 ppm of sodium hexametaphosphate are added to all water pumped from the Ranney wells to act as a stabilizing agent for the dissolved calcium and iron.

DISSOLVED GASES

Were it not removed, the alkaline carbonate content of both the Dana and Savannah River Plant water would lead to a rapid buildup of inert carbon dioxide gas within the GS units, thereby reducing their production in direct proportion to the CO₂ concentration. At both plants the carbonates and bicarbonates are converted to carbon dioxide and removed by adjustment of the water pH to 4.3 followed by vacuum deaeration at a pressure of 30 mm Hg. This treatment reduces the concentration of dissolved carbon dioxide in the GS process feedwater to between 5 and 10 ppm.

Vacuum deaeration also reduces the dissolved oxygen content of the feed from 7 to 10 ppm to less than 0.1 ppm. This dissolved oxygen, if allowed to enter the process, would react with hydrogen sulfide to form elemental sulfur resulting in fouling bubble cap slots, orifices, and heat exchange surfaces in the cold parts of the system.

DISSOLVED IRON AND SILICA

The small concentrations of dissolved iron in the Dana and Savannah River Plant water are not troublesome in themselves; however, in combination with iron bacteria (*Crenothrix*), they have caused iron oxide fouling of the water side of the secondary gas condensers. This problem became sufficiently severe at the Dana Plant to warrant chlorination of the cooling water to the GS units. A continuous chlorine residual of 0.2 ppm is maintained in this water to control the growth of this bacteria. Chlorination has been an effective control, but has not completely eliminated this problem; and it is necessary to periodically flush these exchangers.

The dissolved silica content of the GS process water has not created any problem; however, it remains a potential trouble source in the humidifier section of the hot towers, since insufficient blowdown from this section can raise the silica concentration to the point where it would begin precipitating on the bubble cap slots and trays. For a more complete discussion of solids deposition problems arising from the water chemistry of the two plants, see Appendix E - Corollary Process Problems.

WATER TREATMENT PROCESS DESCRIPTIONS

Schematic representations of the water treatment flowsheets of the Dana and Savannah River Plants are shown in Figures D-1 and D-2. Tables D-I and D-II show the average water analyses at each stage of their respective treatment processes.

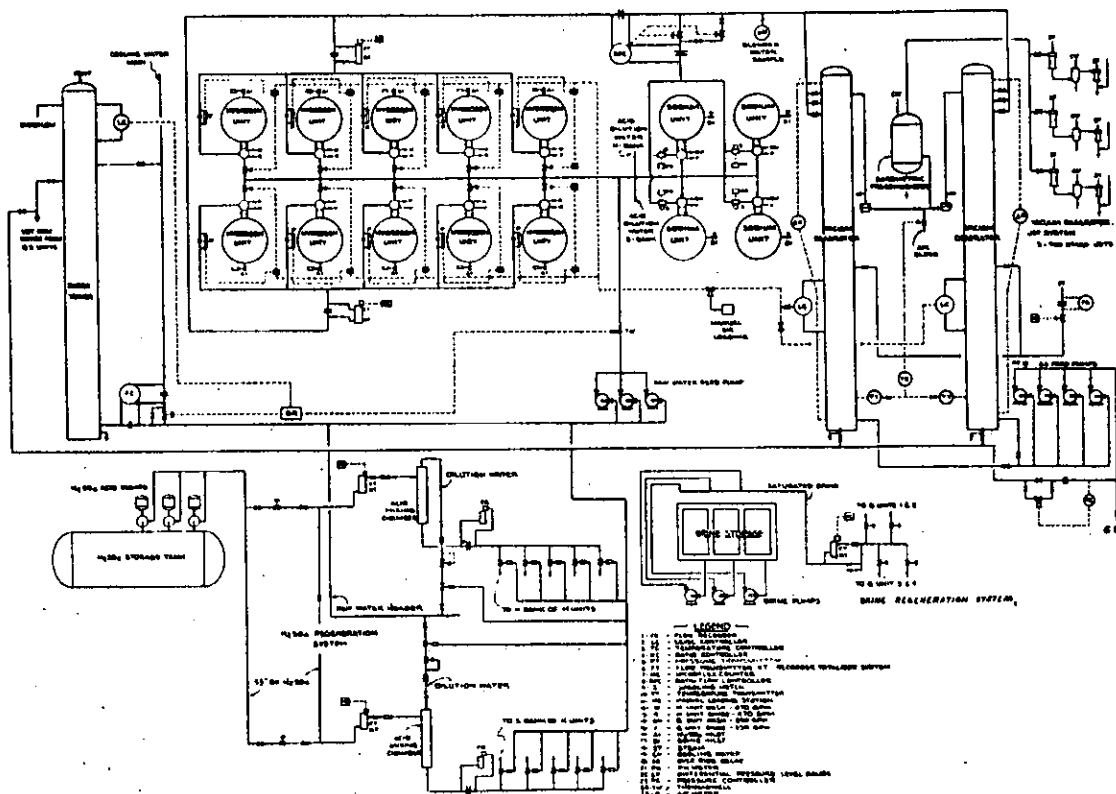


FIGURE D-1 - WATER TREATMENT PROCESS FLOW DIAGRAM - DANA PLANT

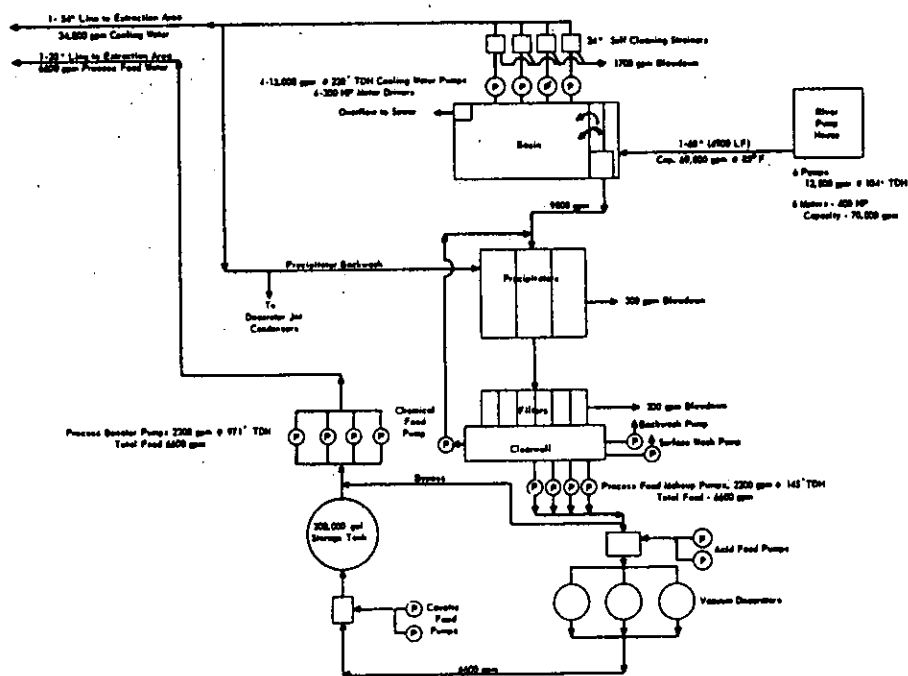


FIGURE D-2 - WATER TREATMENT PROCESS FLOW DIAGRAM - SAVANNAH RIVER PLANT

TABLE D-I

Water Quality - Dana Treatment Process

Constituent	Raw Water		Blended Water 28% Na - 72% H		Deaerated Water	
	ppm		ppm		ppm	
	as CaCO ₃	ppm	as CaCO ₃	ppm	as CaCO ₃	ppm
Calcium ion	216	86.4	0.8	0.4	0.8	0.4
Magnesium ion	104	25.3	0.4	0.1	0.4	0.1
Sodium ion	10	4.6	93	42.8	93	42.8
Bicarbonate ion	237	289	0	0	0	0
Chloride ion	10	7	10	7	10	7
Sulfate ion	60	57.6	60	57.6	60	57.6
Free mineral acidity	0	-	0	-	0	-
Total hardness	320	-	2.0	-	2.0	-
Alkalinity	237	-	0	-	0	-
Free CO ₂	-	19	-	228	-	10
SiO ₂	-	13	-	13	-	13
O ₂	-	9	-	9	-	0.1
pH	7.4		4.3		7.0	

TABLE D-II

Water Quality - Savannah River Treatment Process

Constituent	Raw Water		Clearwell Effluent*		Deaerated Water**	
	ppm		ppm		ppm	
	as CaCO ₃	ppm	as CaCO ₃	ppm	as CaCO ₃	ppm
Calcium ion	5.8	2.3	9.7	3.9	9.7	3.9
Magnesium ion	4.4	1.0	4.4	1.0	4.4	1.0
Sodium ion	20.0	4.6	20.0	4.6	30.0	7.0
Bicarbonate ion	40	24	0	0	0	0
Chloride ion	2.5	0.9	8.5	3.0	8.5	3.0
Sulfate ion	2.3	2.2	31	30	31	30
Free mineral acidity	0	-	4	-	0	0
Total hardness	10.2	0	14.1	-	14.1	-
Alkalinity	38.5	-	0	0	0	0
Free CO ₂	17.0	7.5	57	25	4.5	2
SiO ₂	-	10	-	10	-	10
O ₂	-	9	-	9	-	9
pH	6.9		4.3		7.0	
Turbidity	-	35	-	1.0	-	1.0
Iron	-	0.5	-	0.5	-	0.5
Phosphate	-	0.9	-	0.9	-	0.9

* After pH adjustment for deaeration

** After neutralization of free mineral acidity

APPENDIX E

COROLLARY PROCESS PROBLEMS

This Appendix contains a discussion of a number of process problems that are incidental to, and generally peculiar to, the arrangement of equipment chosen for one or the other of the two plants, or that are otherwise of such a nature that a detailed discussion of them would disrupt the continuity of the general discussion in the body of this Manual.

COLD TOWER TEMPERATURES

The temperature of a cold tower in the GS process is primarily determined by the inlet gas temperature. The inlet water temperature has some effect, but only over the upper 10 to 15 trays of the column. Although the inlet gas temperature fixes the temperature throughout most of the column, it does not fix it at a constant value, but instead there is a linear decrease in temperature from the bottom of the column to about the 55th tray, amounting to a total of 4°C. Above the 55th tray the temperature gradient breaks away from linearity and approaches the inlet water temperature, and it is only in this range that inlet water temperature exerts any appreciable effect on tower temperature.

The gradual drop in temperature over the lower 80% of the column is attributable to the gradual decrease in pressure of the gas as it moves up the tower, which results in cooling the gas by adiabatic expansion. This cooling would amount to about 1°C if no heat exchange took place, however the cooling gas does exchange heat with the water passing down the column causing a magnification of the cooling effect. This effect is analagous to a typical liquid-air machine or other liquefaction process in which countercurrent heat exchange is utilized to obtain very low temperatures from relatively small temperature differences generated by expansion of a gas.

This cooling effect is a significant factor in plant operation since it, and the temperature of formation of the solid H₂S hydrate, place a lower limit on the gas temperature which can be fed to a cold tower. The temperature of hydrate formation at cold tower pressure is about 28.5°C, therefore gas cannot be fed to the column at temperatures below about 33°C without the danger of plugging the column with hydrate unless additional heat is supplied to the middle of the column.

Water is fed to the top of the cold towers at temperatures no lower than 28.5°C to minimize the risk of H₂S hydrate formation. The heat of solution of H₂S raises the water temperature to 34°C within one plate resulting in a positive temperature gradient over the top 20% of the column with temperatures increasing from 28.5°C at the 55th plate to 34°C at the top plate. The net result of the column cooling effect and the heating due to the heat of solution is a minimum

attainable average column temperature of about 31°C, or 2.5°C above the hydrate temperature.

A second thermal effect occurs in higher concentration D₂O cold tower streams due to the heat released in the exchange reaction:



This effect only becomes appreciable in D₂O concentrations above 4%. However in this range it does place a lower limit of 40°C on column temperature of both the fourth and fifth stages of a Dana unit and in the second column of the second stage of a Savannah River unit.

DEPOSITION OF SOLIDS

Solids deposition in various parts of the GS process equipment became a severe and continuing problem at the Dana Plant. The problems were caused primarily by a single factor, i.e., the process towers and internals were manufactured of carbon or 410 stainless steel. By contrast, little difficulty with solids deposition has been encountered at the Savannah River Plant which was constructed with Type 304 stainless-steel-lined columns and Type 304 stainless steel trays.

Iron Sulfide

At Dana, operation of the GS process with carbon steel towers and 410 stainless steel trays containing solution of H₂S in water resulted in corrosion of the equipment and the formation of an iron sulfide scale on all exposed surfaces. The iron sulfide so formed is soluble up to 6 to 10 ppm at cold tower temperatures and a process pH of about 3.5. However, iron sulfide is soluble in inverse proportion to the process temperature and pH. The iron sulfide that dissolved in the cold towers precipitated in the hot towers, waste stripper, and waste stripper heat exchangers. This problem became so severe that during 1953 waste strippers and stripper exchangers were being cleaned on an 8 to 12-week campaign basis resulting in 2 to 3-day unit outages every 3 months.

The problem was successfully eliminated by suppressing the iron sulfide solubility in the columns by a factor of 50 through raising the pH of the process about 0.5 pH units, i.e., from 3.5 to 4.0 in the cold towers and 4.0 to 4.5 in the hot towers. This was done by adding 150 ppm of sodium hydrosulfide or 110 ppm of sodium hydroxide to the process in the feed water. Although the effect of this change was to decrease the solubility of iron sulfide, thereby precipitating a greater percentage of that which did dissolve in the cold towers, the solubility in the cold towers had been reduced by such a large factor that the precipitation of the small amounts which dissolved becomes inconsequential. The waste strippers effluent pH rose to 11.5 as a result of this feedwater treatment, which resulted in a continuous loss of 25 ppm of sulfide in the waste stream regardless of whether NaHS or NaOH was used as the treating agent. Since the loss of sulfide

was effectively an H_2S gas loss, NaHS was used in preference to NaOH since it resulted in a net H_2S gain in the unit rather than a pressure loss. The gain resulted from the fact that the waste stripper recovered 50% of the sulfide in the feed water by steam distillation.

Calcium

The increase in waste stripper effluent pH at the Dana Plant occasioned by addition of 150 ppm of NaHS to the feed water for control of sulfide deposition resulted in precipitation of the 1 to 2-ppm residual calcium concentration in the process water. This deposition took place in the waste stripper and stripper heat exchanger shells. The calcium precipitated as a basic phosphate, calcium hydroxyapatite. The phosphate ion was present in the water though prior treatment of all raw water from the Ranney wells with sodium hexametaphosphate ("Calgon" or "Nalco 680") for the stabilization of iron and calcium in raw water used for coolant in the process heat exchangers. This phosphate ion was not removed by the ion exchange treatment of the feed water.

This calcium deposition was prevented by feeding sulfuric acid to the GS process waste strippers at a rate controlled by the pH of the stripper effluent. The pH control range was 6.0 to 8.0, which prevented the calcium deposition completely and was also effective in reducing the sulfide concentration in the waste to less than 1 ppm, effecting a considerable H_2S gas savings.

As a result of the process water treatment with NaHS and H_2SO_4 sufficient gas was manufactured within the units themselves to make up for all gas losses through leaks, removal of inerts, etc. and the gas generation plant was therefore placed in standby operation except for its function as a gas rundown, storage, and return facility.

Iron Oxide

The deposition of iron oxides occurred at both Dana and Savannah River in all heat exchangers cooled by well or river water. This oxide deposition was found to be caused by the action of iron bacteria (Crenothrix) which collected in the heat exchangers. This deposition problem was effectively controlled, but not completely eliminated, by chlorination of the GS process cooling water with sufficient chlorine to maintain a free chlorine residual in the water of 0.1 to 0.5 ppm.

Periodic checks of the free chlorine residual from each exchanger was also used to pick up any leakage of H_2S into the cooling water. Reaction of the chlorine with H_2S resulted in zero chlorine residuals. At Dana the two units which return warm cooling water to the Water Treatment Plant for use as process feed water could not be chlorinated because free chlorine degrades the resin used in the ion exchange units, and in addition the formation of free sulfur within the units through reaction with chlorine would result in a sulfur deposition problem.

PROCESS HEAT RECOVERY

The GS process steam requirements represent 44% of the direct cost of producing heavy water and 75% of the total utilities cost. It is evident therefore that the mode of operation of the unit heat recovery systems can have a major influence on the production cost of heavy water.

All process heat enters a GS unit as 350 psig steam, half entering through the waste stripper and half added directly to the hot towers. All heat leaving the process leaves in the waste water stream and in the cooling water effluent from the secondary gas cooler-condensers. A total of 175,000 ft² of heat exchange surface and 40 first-stage hot tower plates have been provided in the equivalent of each Dana GS unit to perform the necessary heating and cooling operations with the economic minimum loss of heat.

BASIC PRINCIPLES OF THE HEAT RECOVERY SYSTEM

The GS unit heat recovery system can be broken down into two main sections.

1. The gas heating, humidifying, cooling, and dehumidifying heat recovery loop
2. The waste water and hot tower feed water heat exchange system

The gas heat recovery system consists of a closed cycle water-to-gas and gas-to-water exchange system. The gas leaving the hot towers passes through three heat exchangers in series (two primary and one secondary condenser) in being cooled from hot tower to cold tower temperatures. The gas gives up heat in the primary condensers to a closed circuit water loop. This water is fed to the 10th tray of the hot towers at 115°C where it heats and humidifies the cold gas entering the bottom of the tower. After giving up its heat to the gas the water at 70°C is recirculated to the primary condensers to complete the cycle. Approximately 10% of the water circulating in the loop is removed from the circuit as humidity in the gas stream. This water is made up by adding a portion of the process waste water leaving the 11th tray of the hot tower to the heating-humidifying loop. The gas leaving the primary condensers at 80°C is cooled to cold tower temperature in the secondary condenser. The secondary condenser cooling water which enters at 18°C and leaves at 40°C carries away approximately 80% of the process waste heat.

The process waste water heat recovery system consists of two sets of heat exchangers; the waste stripper feed preheaters (stripper exchanger) and the hot tower feed water preheaters (liquor heaters). Water which has been stripped of H₂S by steam at a temperature of 220°C passes through a series of heat exchangers where it gives up heat to the

water feeding the waste stripper. Leaving these exchangers at 140°C it then passes through a second series of exchangers where it gives up heat to the water leaving the cold towers as feed for the hot towers. After passing through this bank of exchangers the waste water is discarded at about 70°C.

OPTIMUM PROCESS HEAT RECOVERY

The amount of heat recovered in the primary condensers is dependent upon the circulation rate of the humidifier water and the physical condition of the exchanger (fouling, gas binding, etc.). The humidifier water circulation rate also governs the temperature differences between the gas and water streams in both the primary condensers and the humidifier section of the hot towers. It is an important point to recognize that because the rate of circulation of humidifier water governs both of these temperature driving forces, there is an optimum humidifier circulation rate which will recover the maximum amount of heat for any set of process conditions and physical conditions of the heat exchanger surfaces. This optimum can be readily found by varying the humidifier circulation rate until the gas temperature leaving the primary condensers is a minimum. This gas temperature is therefore the criterion of heat economy in the gas circulation system.

The maximum heat recovery in the liquid circulation system is primarily a function of the physical condition of the heat exchange surfaces. However several heat economy measures are evident in this system. Although provisions have been made for bypassing hot waste water around the stripper feed preheaters in order to gain high water feed temperatures to the hot towers, the net effect of such operation is a reduction in heat economy with little gain in production.

Similarly, it is preferable to allow the latter-stage hot tower feed streams to cool down and keep the first-stage hot tower liquid feed hot by passing a disproportionate share of the hot waste water through the first-stage exchangers at the expense of the latter stages. It is also economically justifiable to make provisions for introducing the condensate from the primary and secondary condensers to the hot tower feed stream at a point where the temperature of the streams match, i.e., at a feed point within the hot tower liquor heater exchanger bank.

APPENDIX F

ANALYSIS OF HEAVY WATER

AVAILABLE ANALYTICAL METHODS

The Dana and Savannah River Plants use mass spectrometric and densimetric analyses for the determination of the isotopic concentration of heavy water. The mass spectrometer, by measuring the relative abundance of ions of mass 18, and 19, or 19 and 20, measures directly the concentration of HDO in either H₂O or D₂O. An accurate determination of the density of a purified water sample using a pycnometer also provides a direct measure of the deuterium concentration.

Subsequent to the construction of the Dana and Savannah River heavy water plants, two new methods were developed for deuterium analysis neither of which has been used as yet in the plants. In 1953, it was demonstrated that the absorption of infrared radiation by the HDO molecule at 3 microns provided a sensitive measure of the protium content of heavy water⁽¹³⁾. Either conventional infrared prism spectrometers or nondispersive infrared analyzers can be used for this analysis, and both are capable of determining protium content with a relative precision of better than 1% at deuterium concentrations above 99.5%. The speed of the analysis is comparable to that of the mass spectrometer. Similar techniques have since been used to measure the deuterium content of water at concentrations from normal abundance to 50% D₂O. The relative precision for the heavy water analysis rises from 2% at normal abundance to 0.05% at a concentration of 50%.

The second method, depending upon measurements of the emission spectra of atomic hydrogen, has been developed by H. P. Broida at the U. S. Bureau of Standards⁽¹⁴⁾. Water vapor samples are excited in an electrodeless discharge and the isotopic Balmer lines are analyzed with a recording spectrometer developed and manufactured by the Leeds and Northrup Company. This emission technique has demonstrated essentially the same precision as the infrared absorption method at comparable analytical speeds.

If a new heavy water production plant were to be constructed, these newer analytical techniques should receive serious consideration as the means for process control.

DENSIMETRIC ANALYSIS

The density of a sample of water is a function of the concentration of its components, including the hydrogen and oxygen isotopes and any dissolved or suspended impurities, such as salts or gases. Consequently, to determine deuterium concentration from a measurement of density, the sample must be free of dissolved or suspended impurities, and the concentration of the oxygen-18 isotope must be known.

The normal oxygen-18 concentration in water is about 0.2 mol %, however the distillation train (DW process) performs some separation of oxygen-18, increasing its concentration to about 0.4 mol % in the E process feed material. The concentration of oxygen-18 isotope is determined by equilibrating a sample of water with carbon dioxide gas and analyzing the carbon dioxide with a mass spectrometer for its oxygen-18 content. A factor is then computed to correct the densimetric data for the oxygen-18 contribution. This analysis and determination of the correction factor is done once every three months. Purification of the water samples is accomplished by distillation from an alkaline potassium permanganate solution.

Of the several methods available for the measurement of density, the pycnometric method is best suited to plant control analyses and the preparation of most standard control samples. It is used for analysis of samples in the concentration range from 1 to 95% D₂O. The sensitivity of the method is $\pm 0.02\%$ D₂O but the accuracy is not better than $\pm 0.03\%$ D₂O due to an uncertainty of 30 ppm in the density of pure heavy water. In Table F-I are shown some interlaboratory comparisons of pycnometric determinations of heavy water concentration.

MASS SPECTROMETRY

Mass spectrometric methods are capable of determining directly the concentration of different molecular species in mixtures such as H₂, HD, and D₂; or H₂O, HDO, and D₂O. In 1950, the Consolidated Electrodynamics Corporation developed a special mass spectrometer specifically for the isotopic analysis of water vapor and capable of recording results directly as mol % D₂O or H₂O. Precision measurements that were obtained for this "water vapor" mass spectrometer by replicate analyses of control samples are shown in Table F-II. Except for design features that minimize the adsorption of water vapor on the surfaces of the inlet and analyzing systems, the "water vapor" mass spectrometer is a simplified version of a commercial magnetic mass spectrometer and it operates on the same principles.

Cross contamination of successive samples, or samples and standards, known as "memory", has been a problem in water mass spectrometry. The "memory" of the "water vapor" mass spectrometer has been reduced to an acceptable level by means of a sample introduction system which provides a continuous liquid sample flow; however, it is still necessary to use a standard sample having an isotopic concentration within 7% of the concentration of the unknown to obtain accurate analyses.

The mass spectrometers are used for the frequent analyses below 15% D₂O, that are required for the control of the GS process, and for E process samples that contain more than 95% D₂O. Although the mass spectrometer can be used for any concentration of deuterium in water, several hours of equilibration treatment are required to change the range from low to high concentrations of deuterium because of the "memory" effect.

The range of any one instrument is therefore customarily limited to particular ranges of GS process samples or to E process samples. The plant control laboratories normally have eleven spectrometers analyzing GS samples and two analyzing E process samples. A comparison of heavy water concentrations by the mass spectrometric methods in routine use in two independent control laboratories is also shown in Table F-I.

TABLE F-I

Laboratory Cross-Check Analyses

Results in Mol % D₂O

Sample	Laboratory 1		Laboratory 2	
	Mass Spec.	Pycnometer	Mass Spec.	Pycnometer
1	0.030		0.034	
2	0.074		0.075	
3	0.621		0.629	
4	6.21	6.10		6.13
5	15.72	15.52		15.59
6		65.86*		65.53*
7		90.56		90.44
8	99.75	99.84*	99.76	99.93*
8	99.75**			

* Not corrected for the oxygen-18 isotope

** Nier "3/4" mass spectrometer

TABLE F-II

Precision of D₂O Analyses by Mass Spectrometer

Range Mol % D	Number of Determinations	Precision at a 95% Confidence Limit
0.05 - 0.15	45	0.0046 mol % D
0.5 - 2.0	60	0.028 mol % D
13. - 17.	40	0.10 mol % D
99. - 100.	150	0.02 mol % D

APPENDIX G

ELECTROLYSIS CONTROL IN THE E PROCESS

To satisfactorily control the electrolysis operation in the E process it is necessary to know the average deuterium concentration of the cell residue in each cell row (25 cells) as a function of operating time. Without this information it is not possible to efficiently schedule the cell row shutdown or the burner condensate cut tank changes. Sampling of the operating cells is impractical because of the number of samples required and the hazard to personnel in obtaining the samples. However, a sample of the cell row burner condensate which is readily obtainable, and is representative of the average row operation can be related to the average concentration of the cell residue at any instant in time if the separation factor for the process is known. The following seven factors control the relationship between burner condensate, or cell residue deuterium concentration and the cell row operating time.

- (1) Electrolytic separation factor, alpha
- (2) Deuterium concentration of the initial charge
- (3) Initial charge volume
- (4) Concentration of the electrolyte in the initial charge
- (5) Specific gravity of the initial charge
- (6) Total number of ampere-hours of electricity passed through the cell from the start of the run
- (7) Water vapor and entrainment carried away by the cell off-gas from the start of the run

All of the above factors are either known, analyzable, or controllable in operation of the E process except the separation factor, which depends upon the nature of the cell and the operating conditions. An equation was developed which related the above variables with burner condensate concentration and separation factor. A number of plant electrolysis runs were then made with frequent sampling of the burner condensate, to determine the plant separation factor experimentally. This was done by plotting burner condensate concentration against ampere-hours of operation and comparing the curve obtained with a series of similar curves obtained from the derived equation using the separation factor as a parameter (Figure G-1). It was found experimentally that the E process separation factor is 10 throughout most of the run, falling off to 8.5 near the end of the run.

The derived equation relating the E process operating variables has been found very useful and quite accurate for the prediction of cell row shutdown and cut tank changes. It has been reduced to nomograph form for routine process control purposes using a separation factor of 8.5 (Figure G-2).

A derivation of this equation is given below.

a) Nomenclature

G gallons of initial charge per cell
 S specific gravity of the charge
 K one minus the weight fraction of electrolyte in the charge
 M mol fraction D_2O in the charge
 C total mols D_2O and H_2O charged to the cell
 D_c mols D_2O charged to the cell
 H_c mols H_2O charged to the cell
 D_r mols D_2O remaining in cell residue
 H_r mols H_2O remaining in cell residue
 X_d mol fraction D_2O in cell residue
 X_h mol fraction H_2O in cell residue
 Y_d mol fraction D_2O in burner condensate
 Y_h mol fraction H_2O in burner condensate
 I ampere-hours $\times 10^{-3}$ total electricity consumed from start of run
 P mols electrolyzed per 1000 ampere-hours = 0.0411 mol/cell
 α electrolytic separation factor

b) Given equations $\alpha = \frac{X_d}{X_h} \frac{Y_h}{Y_d}$

$$\ln \frac{H_c}{H_r} = \alpha \ln \frac{D_c}{D_r}$$

$$1 = X_d + X_h$$

$$1 = Y_d + Y_h$$

$$\text{Wt } \% D_2O = \frac{20.0194M}{18.0162 + 2.0032M}$$

c) Derivation $\alpha = \frac{X_d}{X_h} \frac{Y_h}{Y_d} = \frac{X_d}{(1-X_d)} \frac{(1-Y_d)}{Y_d} \quad (G-1)$

$$X_d = \frac{Y_d^\alpha}{1 + Y_d(\alpha-1)} \quad (G-2)$$

$$X_h = 1 - X_d = 1 - \frac{Y_d^\alpha}{1 + Y_d(\alpha-1)} = \frac{1 - Y_d}{1 + Y_d(\alpha-1)} \quad (G-3)$$

Given $\frac{H_c}{H_r} = \frac{D_c^\alpha}{D_r^\alpha}$

$$\frac{H_c}{D_c^\alpha} = \frac{H_r}{D_r^\alpha} = \frac{[C-IP]X_h}{[(C-IP)X_d]^\alpha} = \frac{X_h}{[C-IP]^{(\alpha-1)}X_d^\alpha} \quad (G-4)$$

$$\frac{H_c}{D_c^\alpha} [C-IP]^{(\alpha-1)} = \frac{X_h}{X_d^\alpha} = \frac{1 - Y_d}{[1 + Y_d(\alpha-1)]} \frac{[1 + Y_d(\alpha-1)]^\alpha}{(Y_d^\alpha)^\alpha} \quad (G-5)$$

$$\frac{H_c}{D_c^\alpha} [C-IP]^{(\alpha-1)} = \frac{(1 - Y_d)[1 + Y_d(\alpha-1)]^{(\alpha-1)}}{(Y_d^\alpha)^\alpha} \quad (G-6)$$

For the remainder of the derivation the right half of the above equations is represented by $f(Y_d)$

$$D_c = \frac{8.34\text{GSKM}}{18.0162 + 2.0032M} \quad (G-7)$$

$$H_c = \frac{8.34\text{GSK}(1-M)}{18.0162 + 2.0032M} \quad (G-8)$$

$$C_c = D_c + H_c = \frac{8.34\text{GSK}}{18.0162 + 2.0032M} \quad (G-9)$$

$$IP = C_c - \left(\frac{D_c^\alpha}{H_c} \right)^{\frac{1}{\alpha-1}} \left(f(Y_d) \right)^{\frac{1}{\alpha-1}} \quad (G-10)$$

$$I = \frac{8.34\text{GSK}}{(18.0162 + 2.0032M)0.041122} \left[1 - \left(\frac{M^\alpha}{1-M} \right)^{\frac{1}{\alpha-1}} \left(f(Y_d) \right) \right]^{\frac{1}{\alpha-1}} \quad (G-11)$$

Equation (G-11) is the equation desired and may be used to determine theoretical plots of burner-condensate concentration vs. ampere-hours. It also lends itself to the construction of nomographs for plant operations (see Figure G-1 and G-2).

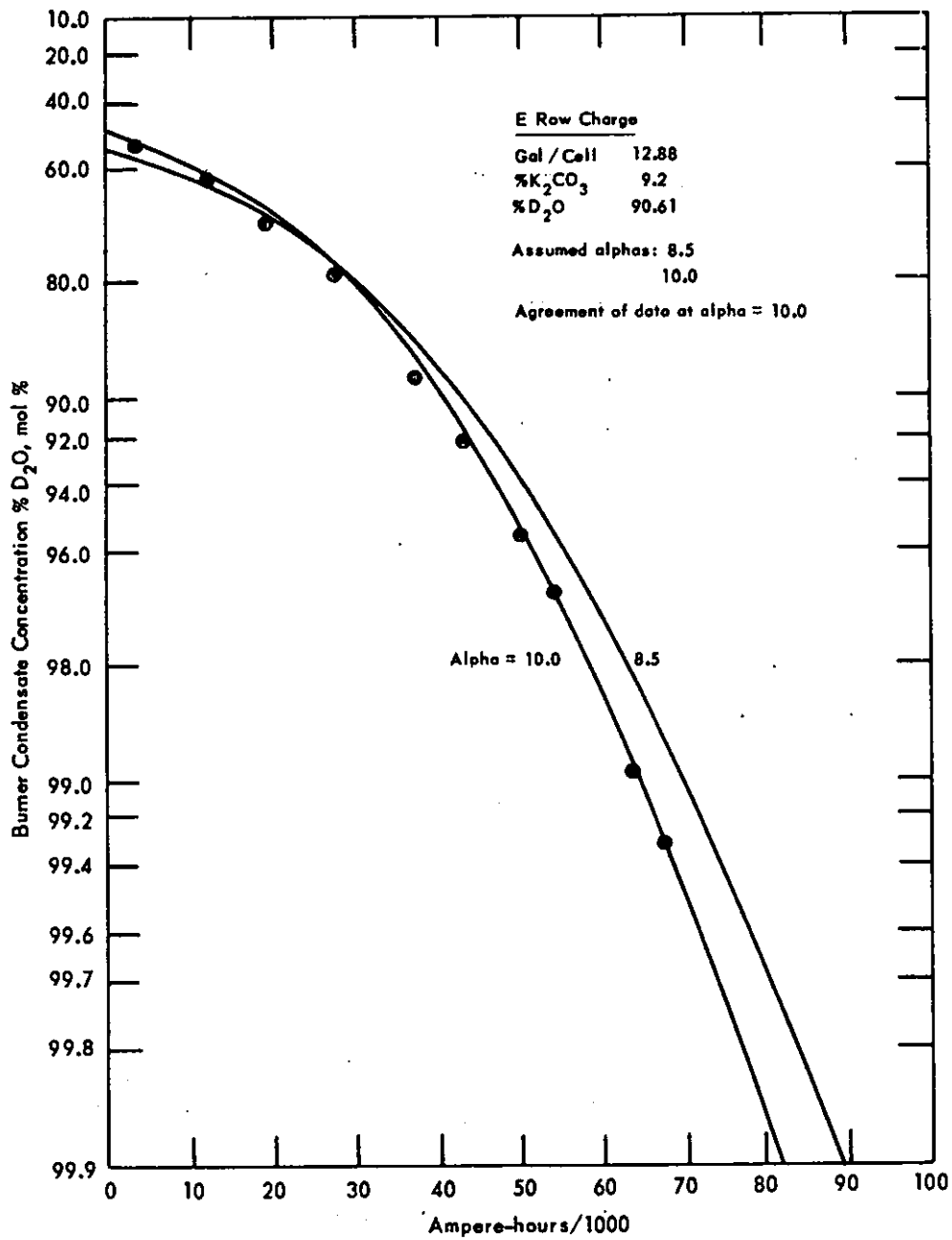


FIGURE G-1 - E PROCESS BURNER CONDENSATE CONCENTRATION vs. AMPERE HOURS OF CELL ROW OPERATION

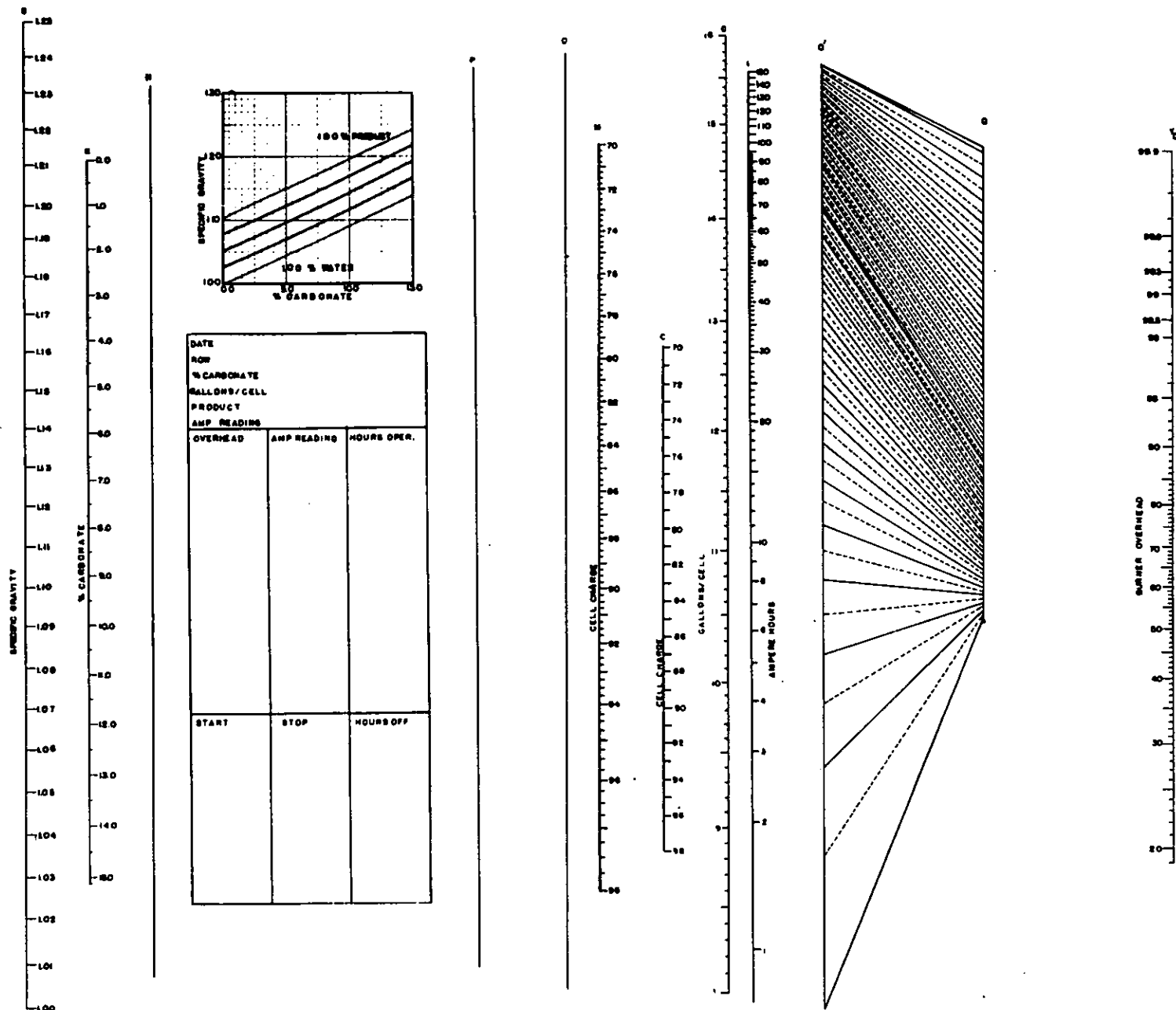


FIGURE G-2 - E PROCESS CONTROL NOMOGRAPH.