AECL-7429

ATOMIC ENERGY OF CANADA LIMITED

L'ÉNERGIE ATOMIQUE DU CANADA LIMITÉE

CANADIAN HEAVY WATER PRODUCTION – 1970 TO 1980

Production d'eau lourde canadienne – de 1970 à 1980

edited by/edité par

M.R. GALLEY, and A.R. BANCROFT

Companion Papers for Presentation at the Second World Congress of Chemical Engineering, Montreal, 1981 October 4-9

Chalk River Nuclear Laboratories   Laboratoires nucléaires de Chalk River

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ATOMIC ENERGY OF CANADA LIMITED

Canadian Heavy Water Production - 1970 to 1980

Companion Papers

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par

M.R. Galley

de la

Société chimique de l'EACL

Résumé

Au cours de la dernière décennie, la capacité canadienne de la production d'eau lourde a progressé depuis la mise en service d'une simple usine en Nouvelle-Ecosse jusqu'à une industrie majeure employant 2200 personnes et exploitant trois usines ayant une capacité de production annuelle globable de plus de 1800 Mg. La réalisation de cette capacité de fonctionnement n'a pas été facile ni totalement dépourvue d'inconvénients mais la détermination de réussir de la part d'Ontario Hydro et de l'EACL a fourni une base de production fiable pour approvisionner en eau lourde les centrales nucléaires CANDU.

La décennie a commencé par une crise naissante dans la fourniture d'eau lourde due à la défaillance de la première usine d'eau lourde de Glace Bay et aux difficultés considérables rencontrées dans la mise en service de la deuxième usine canadienne à Port Hawkesbury. Les leçons apprises à Port Hawkesbury ont été appliquées à l'usine de Bruce où les deux premières unités étaient en construction. Lorsque les unités de l'usine d'eau lourde de Bruce ont été mises en service en 1973, la montée vers la capacité nominale a été très améliorée ce qui a redonné confiance en l'aptitude qu'avait le Canada de réussir à produire de l'eau lourde sur une grande échelle.

Au début des années 1970, il a été décidé de reconstruire l'usine de Glace Bay en ayant recours à un nouvel organigramme et cette usine reconstruite a commencé sa production en 1976.

Deux événements principaux se sont produits au milieu de la décennie: des changements de propriété dans les usines en service et la mise sur pied d'un vaste programme de construction pour appuyer la prévision d'un important programme de construction de centrales CANDU. De nouvelles unités de production incorporant les meilleures caractéristiques de leurs prédécesseurs ont été prévues à Bruce par Ontario Hydro et à La Prade, Québec, par l'EACL.

Le taux élevé de croissance de la demande en électricité ne s'est pas poursuivi et la construction de nouvelles usines a dû être arrêtée. La capacité installée actuelle de la production va probablement suffire pour répondre à la demande d'eau lourde prévue pour la prochaine décennie.

Le développement réussi d'une industrie canadienne de production d'eau lourde a été un exemple d'extrapolation d'un procédé éprouvé utilisant des unités de production relativement petites jusqu'à de grandes usines que la technologie actuelle permet d'appuyer. Alors que de nouvelles usines étaient mises en service, des problèmes technologiques se sont fait jour par suite de la dimension accrue des équipements, mais ces problèmes ont pu être résolus grâce à un important programme de R & D.

Les usines canadiennes ont maintenant produit plus de 7800 Mg d'eau lourde au cours de la dernière décennie à un coût commercialement acceptable, avec un haut degré de sécurité et conformément aux règlements appropriés touchant la protection de l'environnement.

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ATOMIC ENERGY OF CANADA LIMITED

Canadian Heavy Water Production - 1970 to 1980

by

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ABSTRACT

In the last decade, heavy water production capability in Canada has progressed from the commissioning of a single unit plant in Nova Scotia to a major production industry employing 2200 persons and operating three plants with an aggregate annual production capability in excess of 1800 Mg. The achievement of this level of mature operation has not been easy or totally without set-backs, but determination to succeed on the part of Ontario Hydro and AECL has established a reliable production base for supplying heavy water for CANDU Nuclear Power Stations.

The decade opened with an impending crisis in the supply of heavy water due to the failure of the first Glace Bay Heavy Water Plant and considerable difficulty in commissioning the second Canadian plant at Port Hawkesbury. Lessons learned at this latter plant were applied to the Bruce plant where the first two units were under construction. When the Bruce plant units were commissioned in 1973 the rate of approach to design production rates was much improved, renewing confidence in Canada's ability to succeed in large scale heavy water production.

In the early 1970's a decision was made to rehabilitate the Glace Bay plant using a novel flowsheet arrangement and this rebuilt plant commenced production in 1976.

The middle of the decade was marked by two main events: changes in ownership of the operating plants and initiation of a massive construction program to support the forecast of a rapidly expanding CANDU power station construction program. New production units embodying the best features of their predecessors were committed at Bruce by Ontario Hydro and at La Prade, Quebec, by AECL.

The high growth rate in electrical demand did not continue and some new plant construction was curtailed. The present installed production capacity will now probably be adequate to meet anticipated heavy water demand for the next decade.

Development of a successful Canadian heavy water production industry has been an example of scaling-up a demonstrated process, that used relatively small production units, to the largest units that current technology could support. As new plants were brought on line, engineering problems were encountered due to the increased size of equipment but these were overcome through an intensive applied R & D program.

Canadian plants have now produced more than 7800 Mg of heavy water in the last decade at a commercially acceptable cost and with a high degree of safety and compliance with appropriate environmental regulations.

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L'ENERGIE ATOMIQUE DU CANADA, LIMITEE

Avantages pour la production d'eau lourde d'un programme de soutien en R & D

par

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Résumé

Des bénéfices économiques considérables ont été obtenus grâce à un vigoureux programme de R & D tandis que les usines d'eau lourde canadiennes étaient amenées à leur maturité fonctionnelle durant les années 1970. L'implantation au Canada de cette nouvelle industrie chimique a donné lieu à des problèmes inattendus en matière de méthodes, d'équipements et de matériaux. Une petite équipe d'experts techniques travaillant déjà sur les procédés de fabrication d'eau lourde et une plus grande équipe de R & D travaillant dans des domaines connexes ont permis de résoudre rapidement les problèmes limitant la production.

Le nombre des ingénieurs et des scientifiques oeuvrant sur le procédé GS a augmenté rapidement depuis un noyau en 1970 jusqu'à 54 en 1974. Les efforts ont ensuite diminué du fait que les problèmes majeurs étaient résolus et les effectifs n'étaient plus que de 22 en 1980.

L'effort cumulatif au cours de la décennie a été 264 années-hommes à un coût de 3.3% de la valeur de l'eau lourde produite. Les avantages pour la production ont suivi de quelques années les dépenses faites pour les R & D et le taux courant des dépenses est de 1.2% de la valeur du produit.

D'importantes contributions ont été faites dans les domaines suivants:

1. Simulation du procédé: le développement de modèles mathématiques très complexes qui ont permis de décrire les bilans thermiques et les bilans matières sont utilisés pour les analyses de la performance des usines, l'optimalisation du contrôle des procédés, l'analyse des modifications à apporter aux usines et la conception des usines.

2. Chimie opérationnelle: on a procédé au développement de méthodes chimiques analytiques et d'instruments, à la définition du comportement des impuretés, au contrôle du dépôt des solides, au traitement de l'eau et au contrôle des mousses.

3. Matériaux de construction: la mise à l'essai des matériaux possibles, l'analyse des spécimens d'usine, la chimie du système eau-souffre-fer et le développement de méthodes pour former et maintenir des films, ont été des contributions notables.

4. Plateau perforé: la mise à l'essai de plateaux de transfert de masse et de chaleur au laboratoire, l'étude d'une installation pilote et d'une usine de production, le développement de techniques pour mesurer la hauteur et la densité de la mousse et le développement de modèles mathématiques sont à noter.

5. Equipement mécanique: l'application de méthodes d'inspection, la mise à l'essai de joints mécaniques, l'analyse du concept et de la performance des échangeurs de chaleur, ont été des contributions valables.

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Heavy Water Production Benefits of a Supporting R&D Program

by

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ABSTRACT

Considerable economic benefit was obtained from an active R&D program while the Canadian heavy water plants were brought to mature operation during the 1970s. The introduction to Canada of this new chemical processing industry led to unexpected process, equipment and materials problems. Having a small team of technical experts already working on heavy water processes and a much larger R&D team working in related fields allowed a rapid response to the problems that limited production.

The number of engineers and scientists working on the GS process rose rapidly from a skeleton team in 1970 to 54 during 1974. Effort declined steadily as the major problems were solved and reached 22 by 1980.

Cumulative effort over the decade was 264 man-years at a cost of 3.3 percent of the value of the heavy water produced. The production benefits have lagged behind the R&D expenditure by a few years and the current spending rate is 1.2 percent of product value.

Important contributions were made in the following areas:

1. Process simulation; the development of the very complex mathematical models that describe heat and materials balances which are used for plant performance analysis, process control optimization, plant modification analysis and plant design.

2. Process chemistry; the development of chemical analytical methods and instruments, impurity behaviour definition, control of solids deposition, water treatment and foam control.

3. Materials of construction; the testing of candidate materials, analysis of plant specimens, chemistry of the iron-sulphur-water system and development of methods of forming and maintaining protective films.

4. Sieve trays; the testing of heat and mass transfer trays on laboratory, pilot plant and production plant scales, and the development of techniques to measure foam height and density and the development of mathematical models.

5. Mechanical equipment; applying inspection methods, mechanical seal testing, heat exchanger design and performance analysis.

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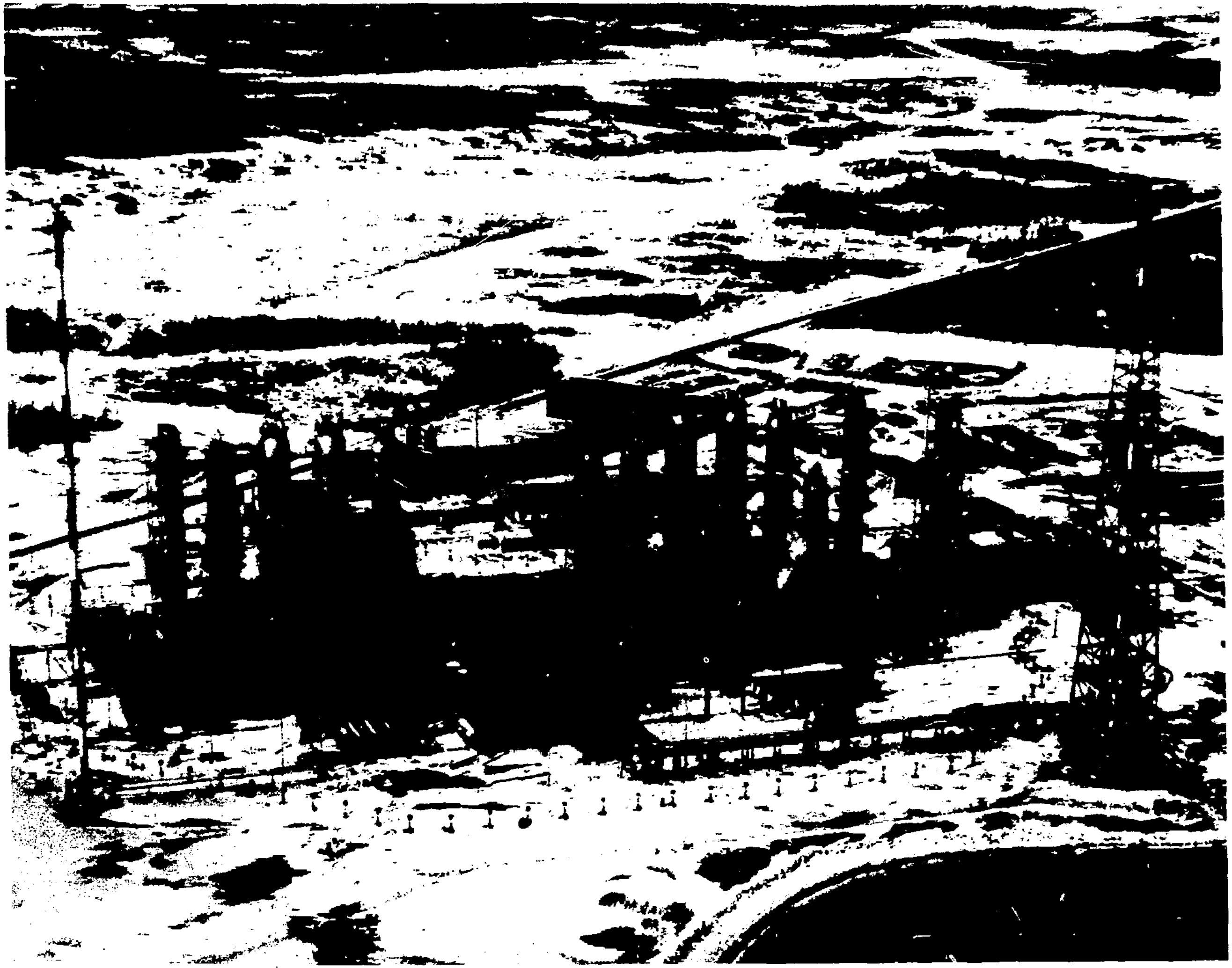
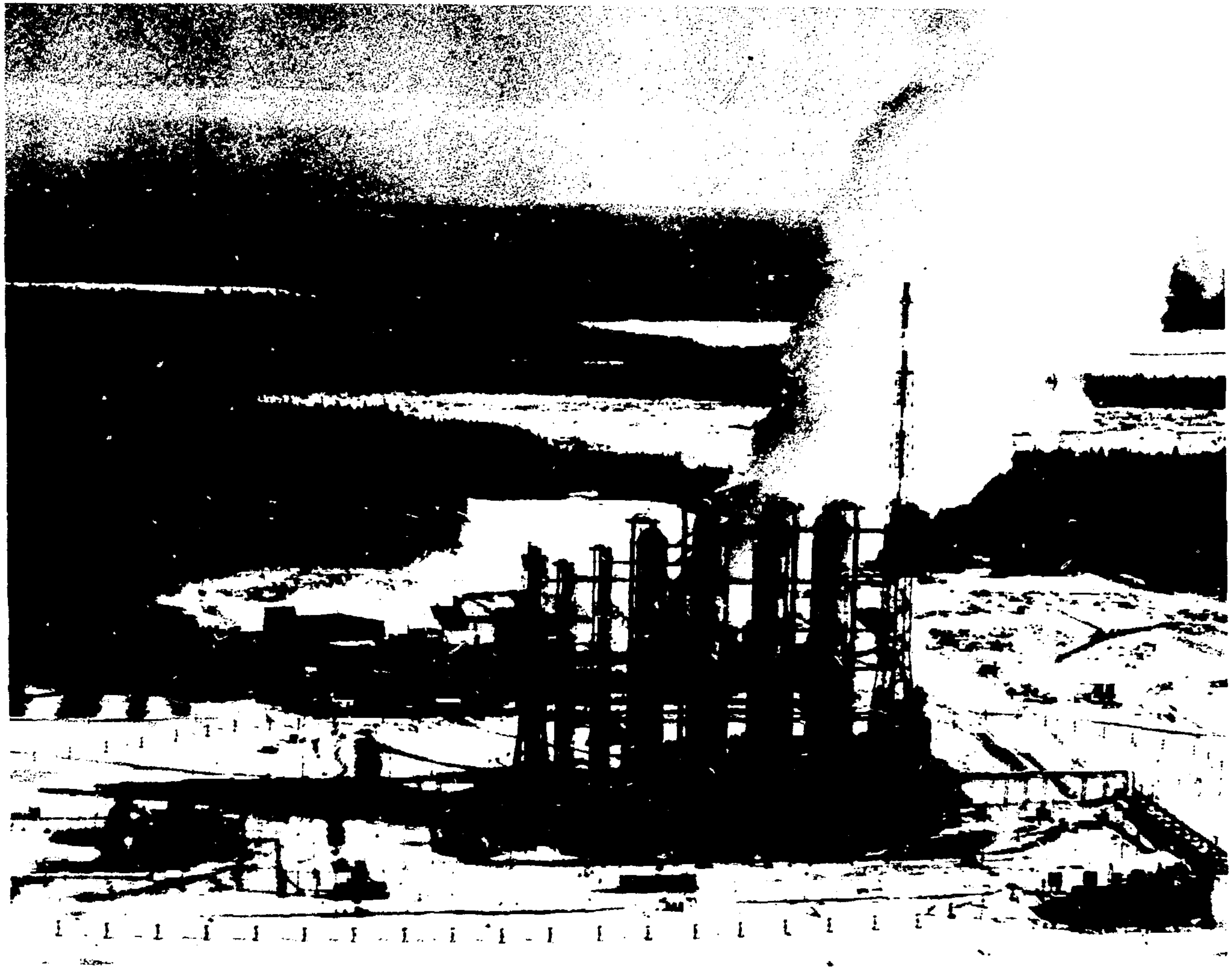
Bruce Heavy Water Plant, Bruce Nuclear Power Development,
Douglas Point, Ontario, owned and operated by Ontario Hydro



Glace Bay Heavy Water Plant, Glace Bay Nova Scotia, owned and operated by Atomic Energy of Canada Limited



Port Hawkesbury Heavy Water Plant, Port Hawkesbury, Nova Scotia, owned and operated by Atomic Energy of Canada Limited

TABLE OF CONTENTS

Canadian Heavy Water Production - 1970 to 1980

Heavy Water Production Benefits of a Supporting R&D Program

Canadian Heavy Water Production - 1970 to 1980

1. INTRODUCTION

This is an account of a major success in the Canadian Chemical Process Industry that has established a supporting infrastructure for one of the world's most successful nuclear power generation systems - CANDU.

The CANadian - Deuterium - Uranium system had its origin in a decision of the Canadian Government, at the end of World War II, to retain the scientific and engineering expertise of the atomic weapons program and re-direct it towards the peaceful uses of nuclear energy. The choice of a nuclear reactor system based on natural uranium and moderated by heavy water was a logical move for Canada because of the experience gained with the NRX reactor at Chalk River. It was also a courageous move because no other country succeeded on this route or devoted their full support to it.

Heavy water power reactor programs were also started in Sweden, Italy, UK, USA, Switzerland and France and in many cases reached the prototype stage before further commercial development ceased. Germany has designed and built two heavy water power reactors and a third is under construction in Argentina. Japan is now planning to go to the demonstration stage with their Fugen reactor.

The United States based their civilian nuclear power program on enriched uranium with light water moderation and the British chose natural uranium moderated by graphite, later switching to enriched uranium, with both systems using carbon dioxide as coolant. Canada saw an advantage in the heavy water system because the high moderating ratio of deuterium allowed excellent neutron economy within the reactor, permitting the use of natural uranium fuel in individual pressure tubes rather than a pressure vessel. Other advantages included more efficient utilization of uranium without any immediate need for reprocessing of spent fuel and the option of using plutonium and thorium fuel cycles if there is a future need to extend reserves of natural uranium.

In the immediate post-war years the United States already had an enormous investment in gaseous diffusion plants for the production of enriched uranium and a much smaller investment in active heavy water production facilities. It was for this reason, together with their experience with highly enriched nuclear submarine reactors, that the U.S.A. chose the enriched fuel route to commercial nuclear power and many other countries throughout the world have adopted this system.

After a somewhat discouraging period in developing prototype reactors, the Canadian approach has been vindicated with CANDU pressurized heavy water reactors now clearly ahead of all competition in terms of on-stream capability or capacity factors. In addition to domestic installations, CANDU reactors are now operating in India and Pakistan and are under construction in Argentina and South Korea. Achievement of this position would not have been possible without the guaranteed supply of heavy water as initial charge for new CANDU reactors.

Heavy water is not consumed in CANDU reactors but about 1% of the initial inventory must be added each year to balance losses due to leakage or down-grading by mixing with light water. Therefore, the required production rate for

heavy water is a direct function of the rate at which new heavy water reactors are constructed, thus making it difficult to match supply with demand, if this construction rate should decline.

This report describes how the Canadian heavy water production industry was established and the difficulties that were encountered in scaling up from the modular small unit plants built in the U.S.A. to the large unit plants that are now operating so successfully in Canada.

2. HEAVY WATER PRODUCTION BEFORE 1970

The isotope deuterium was discovered by Urey, Brickwedde and Murphy(1) in 1931 through fractional evaporation of liquid hydrogen. High purity heavy water (D_2O) was first produced in a laboratory by Lewis(2) using an electrolytic method proposed by Washburn and Urey(3) in 1932. The first heavy water production plant, also based on electrolysis, was built by Norsk Hydro at Rjukan, Norway a few years later. Heavy water production by electrolysis makes use of the fact that a greater proportion of the deuterium (as HDO and D_2O) remains with the electrolyte than is carried away with the hydrogen produced at the cathode. The Rjukan plant was primarily designed to produce hydrogen for ammonia manufacture with heavy water as a by-product. During the German occupation of Norway in the second World War, the plant was modified to recover some additional deuterium from the hydrogen gas streams with the potential of raising production from 1.5 Mg/a to 4.9 Mg/a. Although destroyed by bombing raids in 1943 the plant was rebuilt and is still producing about 20 Mg/a of heavy water.

Work on development of large scale production processes for heavy water in the U.S.A. commenced in 1940, eventually becoming part of the Manhattan District project. A production plant was built at Trail, B.C. in Canada using electrolytic hydrogen from the Consolidated Mining and Smelting Company in conjunction with hydrogen-water exchange. In the U.S.A. three water distillation plants were built by Du Pont at their ordnance works at Morgantown, West Virginia; Childersburg, Alabama and Wabash River, Indiana. The Morgantown plant also incorporated electrolysis for final upgrading of the heavy water. By 1945, sufficient heavy water had been produced for experimental purposes and all the plants, except Trail, B.C., were shut down.

During the 1940-43 period, development work on processes other than water distillation and electrolysis led to the suggestion that dual temperature exchange might be a practical method and work on the hydrogen sulphide-water system commenced at Columbia University. The first flowsheet design for hydrogen sulphide-water exchange was developed in 1942 by J.S. Spevack(4) who was subsequently granted several patents to the process. Development work was abandoned in 1943 because of lack of manpower and anticipated difficulties with materials of construction.

In 1949 the USAEC foresaw a need for large amounts of heavy water and commissioned further study of hydrogen distillation (by the Hydrocarbon Research Corporation) and dual temperature exchange between hydrogen sulphide and water (by the Girdler Corporation). In 1950 Du Pont were engaged by the USAEC to design, build and operate nuclear reactors moderated by heavy water, and also to design, build and operate facilities for fuel fabrication, fuel reprocessing and production of heavy water. For the latter, Du Pont chose the hydrogen sulphide-water process and engaged the Girdler Corporation as sub-contractors to build a heavy water production plant at the Wabash River Ordnance Works near Dana, Indiana. At

this time the process formerly called "S", became known as "GS"; that is, the Girdler version of the sulphide process.

Concurrently with the construction of the Dana Plant, Du Pont built a second facility at the proposed site of the main nuclear complex at Savannah River, S.C. This plant also used the GS process, but with a somewhat simplified flowsheet. Both plants used water distillation followed by electrolysis as the final upgrading step. The GS process was chosen because:

(a) The proven water distillation process was capital intensive and had very high thermal energy requirements.

(b) The hydrogen distillation process was reasonable in operating cost but the technology was incomplete and the adequacy of hydrogen supply was questionable and the sources were scattered.

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

The Dana plant made its first product in mid-1952 and Savannah River at the end of 1952, and both plants were each eventually capable of producing about 500 Mg/a of heavy water. In 1957 the output of the Dana plant was no longer required and it was shut down and partially converted for other uses. Over the next ten years, sections of the Savannah River plant were shut down and dismantled so that today only about one-third of the original plant remains in operation.

During the 28 years of operation at Savannah River, and 5 years at Dana, a vast amount of experience was gained in the operation of the GS process. In 1959, the plant Technical Manual, DP-400[5], was declassified and published; this report was followed by several others and some articles in journals that described operating experience with the process, materials and mechanical equipment, see references (6) to (16).

In addition to the plants in Norway and the U.S.A., several small plants, or pilot plants, were built in other countries. Hydrogen distillation plants were built in Germany, Russia, France, Switzerland and India; ammonia-hydrogen exchange plants were built in France and India and the GS process is being used in India and China. The only plants in this group which have achieved significant production levels are the combined electrolysis/hydrogen distillation plant at Nangal, India; the ammonia hydrogen exchange plant at Mazingarbe, France and plants of unknown type in Russia.

3. CANADIAN HEAVY WATER PRODUCTION PROGRAM

Heavy water production in Canada actually started in 1944 at the Trail, B.C. plant built under the authority of the Manhattan District project. Trail operated until 1956 and produced approximately 50 Mg of heavy water during its lifetime.

When Canada decided to use its experience with heavy water moderated research reactors to develop commercial nuclear power stations in the early 1950's, initial supplies of heavy water were purchased from the USAEC at Savannah River. In the early 1960's it became apparent that an expanding nuclear power construction program would require more heavy water than the USAEC could supply and so the Canadian Government invited proposals for construction of heavy water plants in Canada. With one exception, the proposals received were for plants based on the demonstrated GS process. AECL contracted to purchase the output of a nominal 200 Mg/a plant to be built by Deuterium of Canada Limited (DCL) at Glace Bay, Nova Scotia. While this plant was under construction, the nominal capacity was doubled to 400 Mg/a. In addition AECL entered into a second heavy water purchase agreement with Canadian General Electric (CGE) who started construction of a nominal 400 Mg/a plant at Port Hawkesbury, N.S. Both of these plants were sited on Cape Breton Island because of the availability of power, reasonably high isotopic feed water[26] and local financial incentives.

The process design for the DCL plant at Glace Bay was conceived by J.S. Spevack, one of the original inventors of the GS process. Detailed engineering was performed by Burns and Roe Inc. and construction was carried out by Brown and Root Inc. DCL had considerable difficulty raising capital for their Glace Bay plant and the Province of Nova Scotia assumed more and more financial responsibility. Financial problems, labour and management difficulties, escalating costs, and a variety of technical problems plagued the project. Initial attempts at start-up were made in 1968 but failed due to equipment problems. A second and final attempt was made in 1969. At this point, ownership and control of the plant was assumed by the Province of Nova Scotia who then sought help in rehabilitating the plant. After the plant had remained idle for several years, the Federal Government agreed in 1970 to finance its rehabilitation and, in 1971, AECL were instructed to oversee the project and then operate the facility. A consulting engineering company, Canatom MonMax (now Canatom MHG), was engaged to re-design and rebuild the plant starting in 1972 and first heavy water production was achieved in 1976.

It is of interest to note at this point that, until about 1968, AECL had virtually no in-house experience of the design and operation of GS process heavy water plants. It was expected that private industry could supply the heavy water market by providing capital, building plants and operating them to produce heavy water for sale to AECL. The incentive would be long-term supply contracts at a guaranteed price. It had been assumed that, with about 15 years operating experience at SRP, the technology was demonstrated and there was no need for further process and equipment development. As a result, the designs of the DCL plant at Glace

Bay and the CGE plant at Port Hawkesbury were not reviewed in detail by AECL because no major scale-up problems were anticipated. However by 1969 it had become evident that problems were arising in several areas and R&D activities on the GS process were initiated at the Chalk River Nuclear Laboratories (CRNL) of AECL.

An additional motive for greater involvement in technical support for the GS process was AECL's decision in 1969 to build a third heavy water plant adjacent to the Douglas Point CANDU power station in Ontario, at what was to become the Bruce Nuclear Power Development. It was agreed with Ontario Hydro that AECL would finance and supervise the construction, by the Lummus Company of Canada Limited, of units E1 and E2 of the Bruce Heavy Water Plant (BHWP) and that the facility would be operated by Ontario Hydro using steam from nuclear reactors. In view of the prospects of more success from the Port Hawkesbury plant than from the DCL plant at Glace Bay, AECL chose to duplicate the Port Hawkesbury design at the BHWP, with only minor modifications.[36]

The Port Hawkesbury heavy water plant used a flowsheet that was based on the proposal of Proctor and Thayer [11] published in 1962, but scaled up in unit size and with a steam supply integrated with the adjacent Point Tupper generating station of the Nova Scotia Power Commission. Detailed engineering design was performed by the Lummus Company of Canada Limited (LCCL) and arrangements were made for consulting services to be provided by personnel experienced in the design and operation of the USAEC Dana and Savannah River Plants. The LCCL design team, assembled for the Port Hawkesbury project, were able to follow on with the engineering and construction of the Bruce Heavy Water Plant (BHWP), thus providing good continuity in design. A member of the consulting team from Savannah River was attached to BHWP following start-up experience at Port Hawkesbury and this provided a valuable link for transfer of know-how to the BHWP project.

Port Hawkesbury started production in October 1970 and was followed by unit E1 of BHWP in December 1972 and E2 in May 1973. The experiences gained from starting up Port Hawkesbury were transferred where possible to BHWP by agreement between Canadian General Electric, Ontario Hydro and AECL and there was considerable training of OH personnel undertaken at Port Hawkesbury and at Savannah River through the technology exchange agreement with the USAEC.

Thus Canada's first domestic heavy water production, after Trail, B.C., commenced in 1970 and built up steadily over the next few years. A description of some of the engineering problems encountered, and how they were overcome, is in a later section.

At the time the first BHWP units E1 and E2 were being commissioned in 1972/73, it became apparent that further new heavy water plants, beyond the rehabilitated Glace Bay plant, would be needed to meet the demand forecast for the 1980-2000 period. Ambitious[10] plans to install 133,000 MWe of nuclear power in Canada by 2000, coupled with disappointing early

production levels at Port Hawkesbury and BHWP, led to the commitment in late 1973 of Units B, C and D at Bruce and an AECL plant at La Prade, Quebec. These four plants were each to be of 800 Mg/a nominal capacity, equivalent to BHWP-A (E1 and E2) and double the size of Port Hawkesbury where the nominal design rating was 400 Mg/a.

Prior to the time when these new commitments were made in 1973, the Bruce-A plant was declared "in-service" and purchased by Ontario Hydro from AECL. Later, in 1976 the CGE plant at Port Hawkesbury was sold to AECL and the industry had then devolved to the situation where heavy water production for Ontario Hydro nuclear stations would come exclusively from the BHWP and the remaining domestic and off-shore needs would be met by the AECL owned and operated plants at Port Hawkesbury, Glace Bay and La Prade.

In the later 1970's, partly as a result of reduced industrial growth following the 1973 oil crisis, the annual growth rate in electrical demand in Canada, traditionally 7% per annum in Ontario and Quebec, started to decline. There followed a succession of downward revisions to the estimates of installed nuclear capacity expected in Canada by 2000 and to the estimates of CANDU sales worldwide. Meanwhile by 1976 BHWP-A had demonstrated the capability to perform close to design capacity. This led to a more optimistic forecast of heavy water supply. As a result the heavy water plant construction program underwent continual reassessment and change.

Design and construction of the La Prade heavy water plant by AECL in Quebec was slowed in 1976, revived in 1977 and finally terminated in 1978. The La Prade plant has now been mothballed at 40% completion and the project is not likely to be resumed before 1985 at the earliest. At the BHWP site, Ontario Hydro cancelled Bruce-C and have mothballed BHWP-D at 70% completion but BHWP-B has been completed and is now being commissioned. Thus by 1980 Canada has operating heavy water plants at Bruce, Ontario; Port Hawkesbury and Glace Bay, Nova Scotia. A summary of the chronology of their development and their present status is given in Fig. 1.

Regulation of the operation of all Canadian heavy water plants is the responsibility of the Atomic Energy Control Board (AECB) because heavy water is a prescribed substance under the Canadian Atomic Energy Control Act. The AECB issues annual operating licences to each plant after ensuring that all necessary safety standards have been complied with for the protection of the public. The AECB also maintains a similar close scrutiny of heavy water plant operations as they apply to other nuclear installations. In addition to satisfying the AECB requirements, all heavy water plants are subject to the normal regulations governing the operation of chemical plants in Canada, as imposed by the Department of Labour and appropriate environmental authorities.

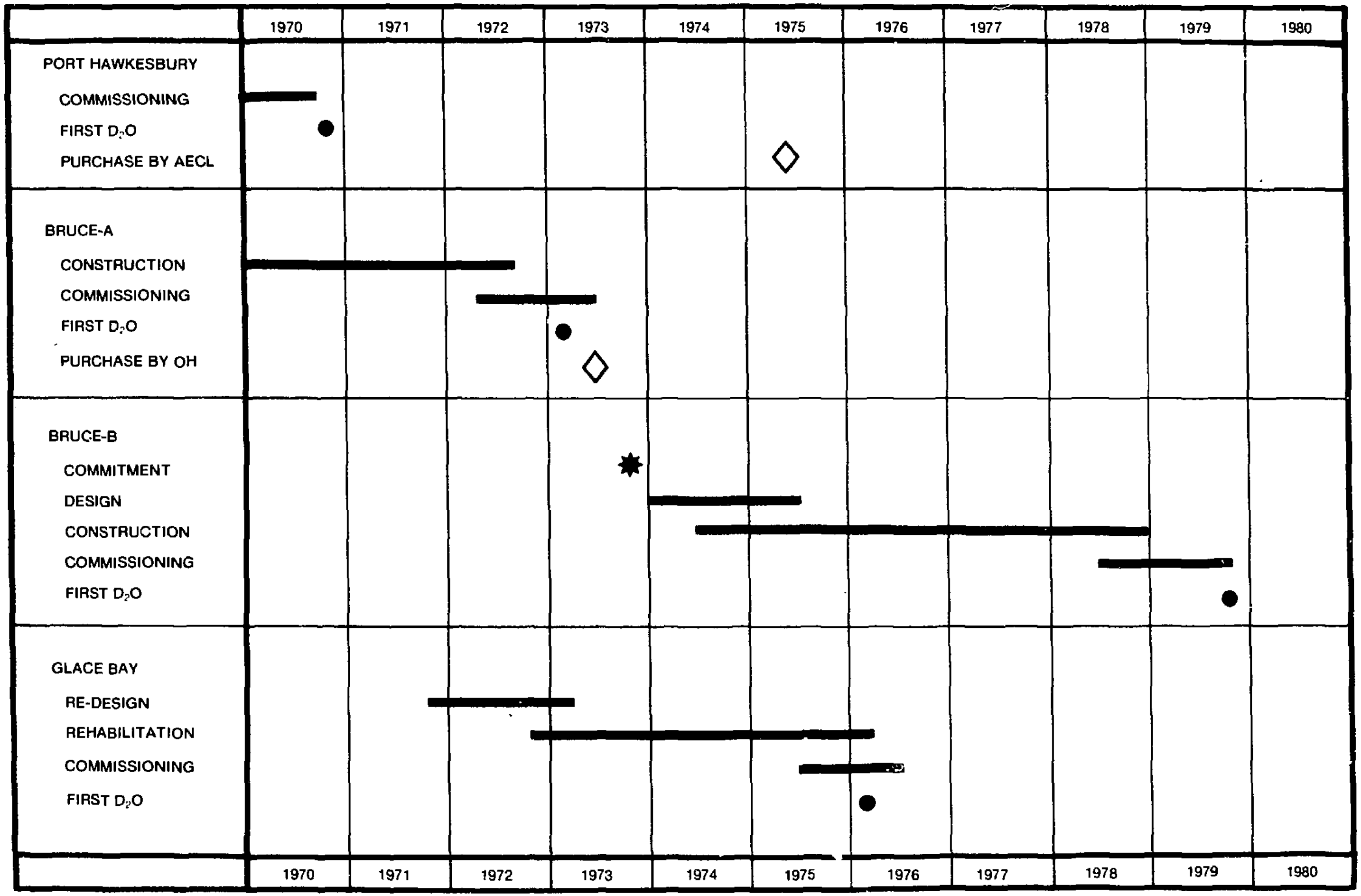


FIG. 1. CHRONOLOGY OF CANADIAN HEAVY WATER PLANT DEVELOPMENTS — 1970 TO 1980

4. THE GS PROCESS

The object of the GS process is to extract deuterium, which occurs in natural water[26] as the molecule HDO where the ratio of D to (D+H) is approximately 1:7000, and then by successive exchange reactions at different temperatures, to produce heavy water, D_2O, of 99.8% purity.

The principle of the separation and enrichment process is based on the fact that, although deuterium and protium (hydrogen of atomic weight 1) have similar physical and chemical properties, the equilibrium constants for isotope exchange reactions vary markedly with temperature. In the hydrogen sulphide-water system, deuterium always prefers to be associated with water to a greater extent than with hydrogen sulphide. The exchange reaction takes place between dissolved hydrogen sulphide and liquid water, and because the system is ionized, no catalyst is needed. At low deuterium concentrations, the reaction $HDS + H_2O \rightleftharpoons H_2S + HDO$ has an equilibrium constant,

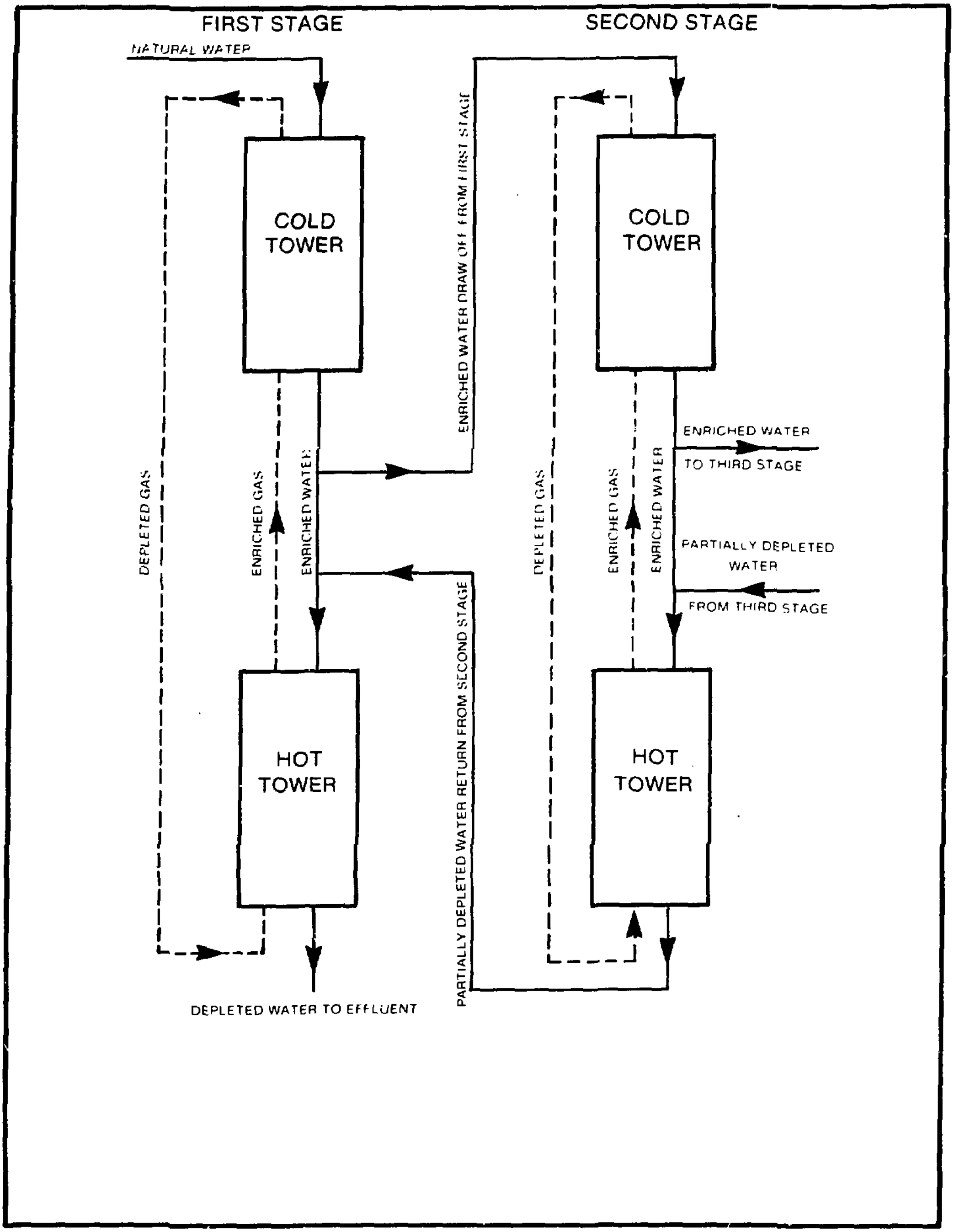
$$k = \frac{(H_2S)}{(HDS)}\frac{(HDO)}{(H_2O)}$$

which approximates to the separation factor α where:

$$\alpha = \frac{(D/(D+H))\ H_2O}{(D/(D+H))\ H_2S}$$

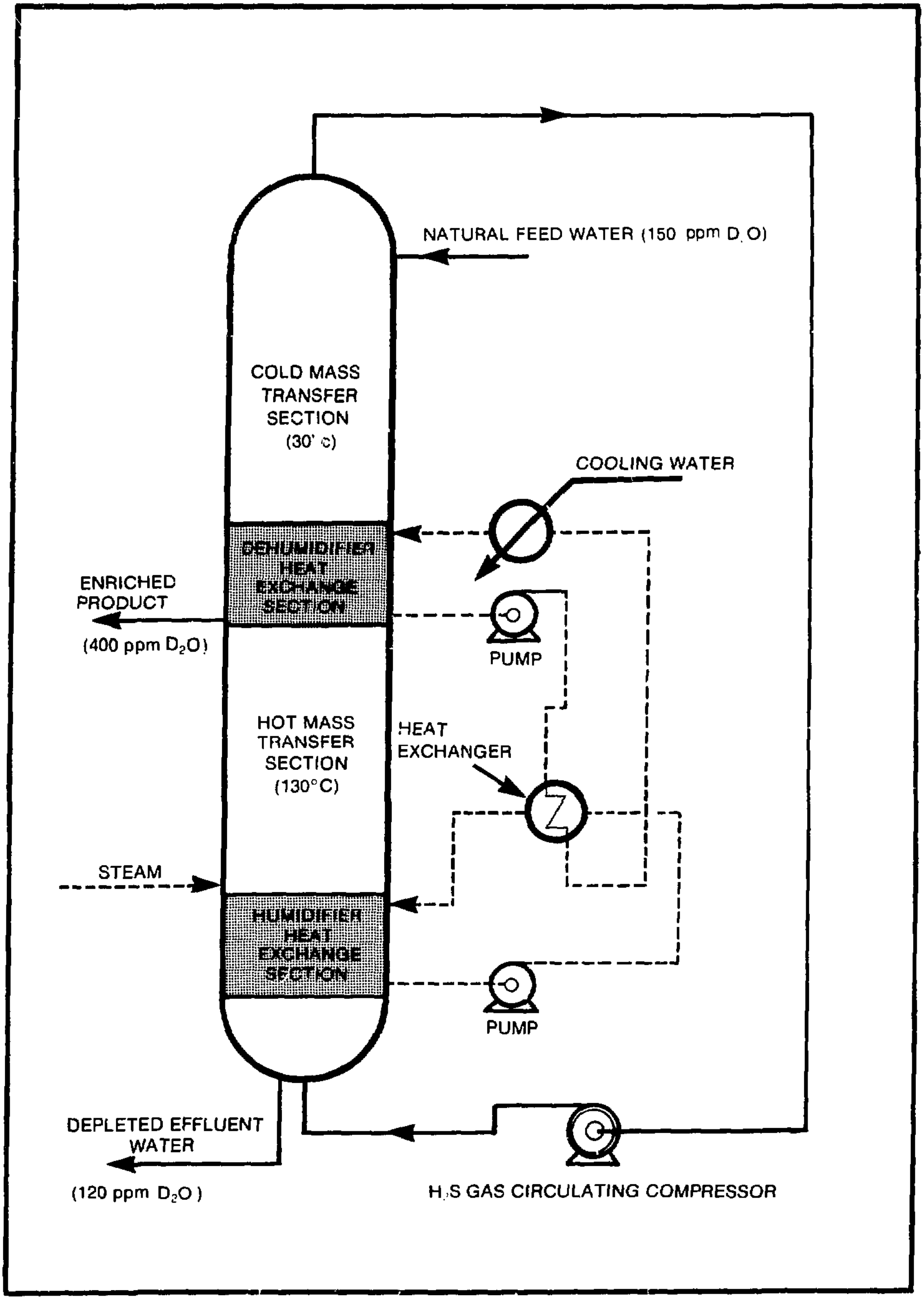
The value of α is always greater than unity, but varies with temperature and it is possible to set up a process system operating at two distinct temperatures so that, at the lower temperature, deuterium will transfer from the gas phase to the liquid phase and the reverse will occur at the higher temperature. Using the counter-current contacting arrangement shown in Fig. 2, where the recirculating gas flow is in a certain fixed ratio to the liquid feed flow, the water becomes enriched in deuterium as it flows down the cold tower and then becomes depleted as it flows down the hot tower. Provided the flow ratios are set correctly and there is net removal of enriched liquid from the bottom of the cold tower, the water leaving the bottom of the hot tower will be depleted to below the naturally occurring concentration of deuterium.

A typical single first stage tower of a GS process plant is shown in Fig. 3 following the hydrogen sulphide gas circuit, from the discharge of the recirculating blower the gas enters a humidification section where it is raised to hot tower temperature by counter-current contact with the down-flowing water, on which is superimposed an additional recirculating flow of hot water. Steam may be added at the top of the humidification section to make a final adjustment to the desired hot tower gas temperature. Deuterium exchange from liquid to gas occurs in the long hot tower section which is made up of a series of conventional sieve trays. Above the hot tower section is a dehumidification section where the gas is cooled down to cold tower temperature, again assisted by an additional recirculating flow of cooled water. The cold tower section where deuterium exchanges from gas to liquid is of similar size to the hot section and also contains many sieve trays. Frequently these various sections are stacked on top of each other in a single tower shell as illustrated.



GIRDLER SULPHIDE DUAL TEMPERATURE PROCESS

FIG. 2.



TYPICAL FIRST STAGE GIRDLER SULPHIDE TOWER
FIG. 3.

Treated feedwater is fed directly to the top of the cold tower section and enriched water or gas is withdrawn near the bottom of this section and fed forward to a second stage for further enrichment, being replaced by a flow of depleted material from this second stage. At the bottom of the humidifier section, water depleted below natural concentration is withdrawn, stripped of dissolved hydrogen sulphide and discharged as effluent.

The operating conditions of the bithermal exchange tower, described above, are constrained by certain physical properties[27] of the hydrogen sulphide-water system, otherwise it would be advantageous to operate with hot and cold tower temperatures as far apart as possible to maximize the difference in separation factors and so reduce the number of theoretical plates required to effect a given separation.

The maximum operating pressure is limited to about 2150 kPa because hydrogen sulphide gas liquefies near ambient temperature (30°C) and 2250 kPa. The minimum cold tower temperature is dictated by the formation of an ice-like hydrate between hydrogen sulphide and water which occurs at 29.1°C at 2150 kPa. The maximum hot tower temperature is an economic consideration because, as the temperature rises at the fixed operating pressure, the partial pressure of water vapour rapidly becomes significant, requiring increases in equipment size to handle the gas volume and increases in energy requirements to vapourize water.

For the above reasons, GS process plants built to date generally operate at 2150 kPa pressure, or less, and tower temperatures of 30°C (cold) and 130° to 140°C (hot). Another property of the hydrogen sulphide-water system, namely the tendency to foam when agitated, also sets a limit on the superficial gas velocity that can be attained through an exchange tower equipped with sieve trays. The maximum fraction of deuterium that can be recovered from raw feed water is limited by the ratio of cold and hot exchange separation factors to about 21% but this recovery would require an infinite number of theoretical plates. In practice, plants are designed for 19.5% recovery or less, depending upon the flowsheet arrangement chosen.

Therefore, a plant to recover about 50 kg/h of heavy water (D_2O) would require a feedwater flow rate of about 425 kg/s. The corresponding hydrogen sulphide gas circulation flow rate is fixed by process requirements and, together with the maximum allowable superficial velocity, this determines the cross-sectional area needed for the first stage of the process. For 50 kg/h production, this area is approximately 170 m^2 and corresponds to three 8.5 m diameter first stage towers operating in parallel. When the Port Hawkesbury plant was designed, it was considered that an exchange tower of 8.5 m diameter and 75 m height was the maximum size of vertical pressure vessel that could be built with current technology. The height of 75 m determines the number of sieve trays that can be installed which in turn sets the degree of isotopic enrichment attainable at a specified recovery rate. Towers of this size typically enrich in the range 4 to 6 times natural concentration, so second and third stages are needed to obtain about 20% of D_2O. Above this concentration,

further enrichment is carried out by distillation of (heavy) water rather than by the GS process because distillation is simpler and the low operating pressure reduces the risk of product losses through leakage.

From the foregoing brief description of the process it may be seen that some of the key areas of design of GS process plants include:

- Provision of at least 425 kg/s of treated fresh water.
- Large vertical pressure vessels to serve as exchange towers.
- Sieve trays to promote intimate counter-current contact of hydrogen sulphide and water under hydraulically stable conditions.
- Supply of process steam and cooling water.
- A heat exchange network to minimize steam consumption.
- Process control system.
- Safety and environmental systems capable of handling an inventory of about 600 Mg of toxic hydrogen sulphide.
- Materials capable of withstanding the corrosive hydrogen sulphide-water system.

5. CANADIAN HEAVY WATER PLANT PERFORMANCE

5.1 Port Hawkesbury Heavy Water Plant

This is a single unit plant of nominal 400 Mg/a capacity consisting of three parallel first stage towers, a single second stage followed by a third stage and a water distillation unit. The second and third stages are not capable of independent operation, being reliant upon operation of the preceding stage for their supply of circulating hydrogen sulphide gas. Second stage operation can only be sustained if at least two of the three first stages are in operation. This arrangement, as shown in Fig. 4 , has advantages in terms of heat economy because no additional heat has to be supplied to the second and third stages.

Construction of this plant by the Lummus Company of Canada Limited (LCCL) on behalf of Canadian General Electric (CGE) started in 1966 and first production began in the Fall of 1970.[22] The plant had been commissioned successfully using nitrogen in place of hydrogen sulphide, but at reduced pressure to give representative sieve tray F-factors.

When operation with hydrogen-sulphide commenced, production of reactor grade heavy water was achieved within a few weeks, but at a low rate and with considerable operational difficulties.

During the first few years of operation, the following serious problems were encountered:

- The upper first stage hot tower trays fouled rapidly with iron sulphide, almost to the point of total blockage. This occurred because there was only rudimentary treatment of the fresh feedwater which was found later to contain a high level of dissolved iron. Iron sulphide is less soluble at hot tower conditions than at cold and so it deposited on the hot tower trays. The problem was ultimately solved by installing a conventional alum clarifier which removed the iron by flocculation.

- Operation at design flows and pressures could not be achieved because of severe hydraulic instability in the cold tower sieve trays and dehumidifier region. This was partially relieved by improvements in water treatment, alteration of sieve tray weir heights and addition of antifoam, but a final solution was not found until 1978, when it was discovered that certain transfer trays were accumulating foaming agents. These transfer trays were not installed in the similar BHWP Units and so the problem was not encountered with the same severity at that plant.

- Many heat exchanger tube failures were encountered, due to pitting during shutdown conditions, and it was found that certain grades of stainless steel were particularly susceptible to this type of failure. When tubes were replaced by the correct grade of steel, these failures ceased.

- Integration of the feedwater and cooling water systems, to effect feedwater pre-heating without the use of heat exchangers, led to

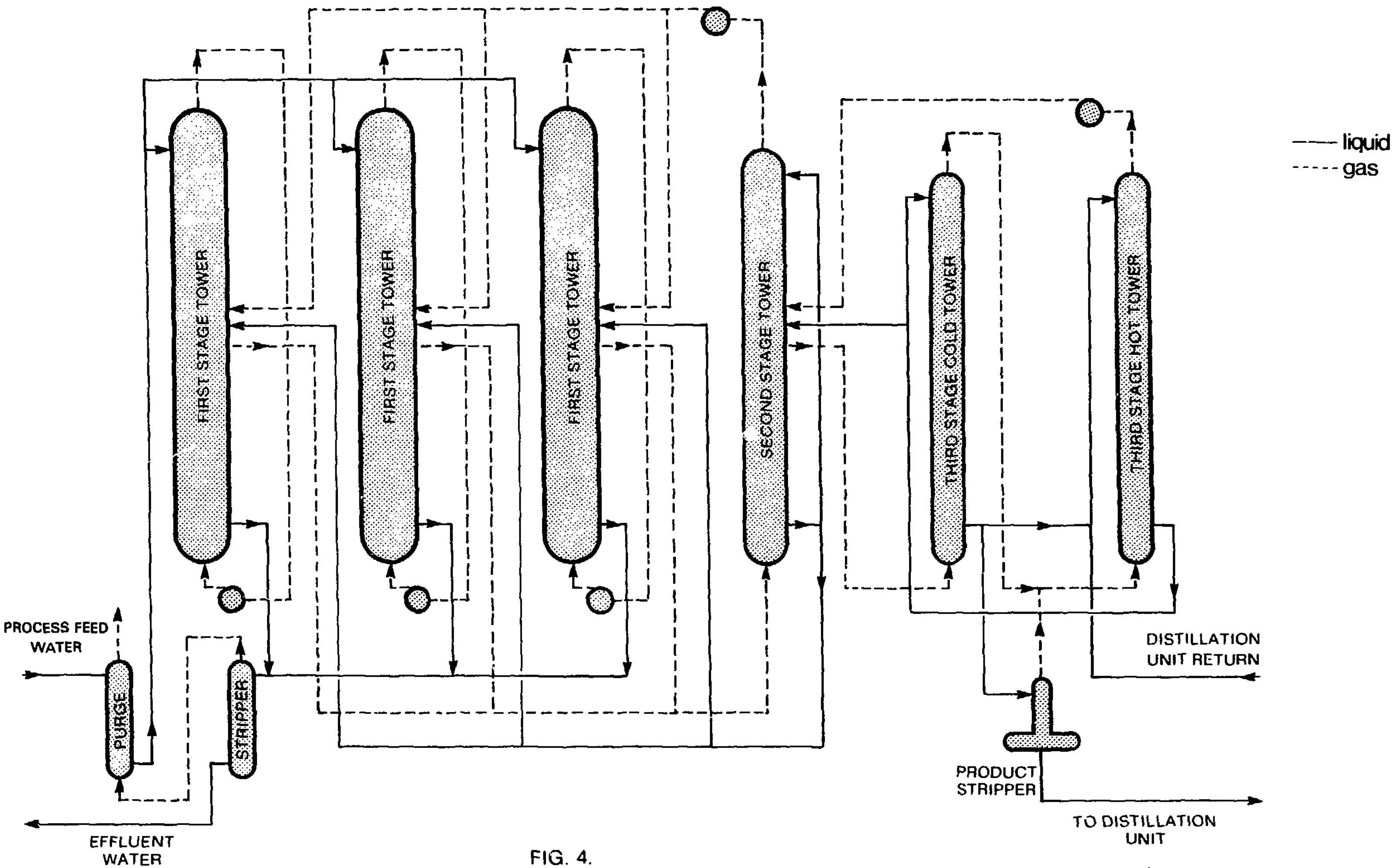


FIG. 4.
GIRDLER SULPHIDE PROCESS
PORT HAWKESBURY/BRUCE HWP UNIT

incompatible water treatment requirements for the two services. Careful selection of additives to minimize cooling water circuit corrosion has improved operation by reducing deposition of corrosion inhibiting chemicals in the GS process systems.

- Achievement of design D_2O concentrations in the third stage system was impossible because no provision had been made for the removal of the heat of exchange reaction. Consequently the water distillation (DW) finishing unit was undersized with respect to the achievable feed concentration. This problem has been partially counterbalanced by operation of the GS first stages in excess of design flows and by withdrawing D_2O product at less than reactor grade isotopic for final upgrading elsewhere.

The manifestation of these and other problems led to the initiation of the large and diverse GS process R&D program at AECL's Chalk River Nuclear Laboratories (CRNL), details of which are given in a companion report (17). In parallel with the CRNL program an extensive R&D program was also launched by the Schenectady laboratories of G.E. in the U.S.A.

As the problems were steadily eliminated, annual production levels rose as shown in Table 1 reaching 294 Mg in 1974. Although some further equipment problems were encountered, including a failure of the steam line from the Point Tupper power station, the determined efforts of the operating and maintenance staff were rewarded by improved production. During the 1974 to 1978 period the results of the GS process R&D program began to be applied to plant operations with increasing benefits.

Operation from 1978 onwards has been much improved due to clearance of a backlog of maintenance items and elimination of a bottleneck caused by superfluous transfer trays. Considerable effort on development of control strategies through simulation studies has resulted in reduced production losses and improved efficiency of energy utilization.

Since the construction of the Port Hawkesbury plant in the late 1960's, the Atomic Energy Control Board (AECB) have revised their guidelines with respect to siting of GS process plants and now require a larger exclusion area around the plant periphery unless alternative means are used to disperse a potential major escape of hydrogen sulphide gas. In order to comply with these regulations, the Port Hawkesbury plant has recently installed a gas dispersion system (GDS) which consists of a ring of propane burners encircling the plant which are automatically ignited by sensors detecting an abnormal level of hydrogen sulphide. These burners create a thermal updraft which will assist in dispersion of the toxic hydrogen sulphide.

5.2 Bruce Heavy Water Plant

Construction of units E1 and E2 of the Bruce plant, which later became

collectively known as BHWP-A, was initiated in 1969 and commissioning began in 1972.[23] Units E1 and E2 are each self-contained production facilities of 400 Mg/a nominal capacity and very similar in design to the Port Hawkesbury plant. Certain changes were made to the design of purge, stripper and effluent systems with both BHWP units sharing common services such as feed water supply, steam supply, cooling water distribution and final upgrading by water distillation.

When Unit E1 was first started up in 1972 November, process control was extremely difficult and production of heavy water was limited to about 40% design. The operation was characterized by frequent and severe instabilities caused by foaming on the trays of the first stage towers. A deliberate decision not to use antifoam had been made because experience at Port Hawkesbury, and research at CRNL and G.E. Schenectady, had already raised doubts as to the efficacy of the silicone based antifoam then in use. However, by 1973 June, the instabilities persisted and antifoam addition was begun. The operation improved and extraction increased quickly to about 73% of design.

In 1973 April the outlet weirs of trays in Unit E2 were reduced in height in order to lower froth levels and accommodate the foamy situation. This decision was based on experience gained in the early operation of E1 and Port Hawkesbury and comparison with sieve tray experience at SRP. The modification was successful and resulted in more stable operation of E2 than E1. The weir heights in E1 were similarly reduced in 1973 September and extraction increased to 93% of design. The original design of BHWP-A feedwater treatment system only provided coarse screens and sand filters for treatment of the relatively clean feedwater from Lake Huron. During construction, the feedwater problems at Port Hawkesbury assumed prominence and it was considered prudent to install clarifiers at BHWP-A even though Lake Huron water had a very low dissolved iron content. It was thought that clarifiers may be necessary at BHWP-A to reduce turbidity because SRP felt that turbidity was one of the prime causes of foaming instabilities. By 1974 it was clear that operation with alum clarifiers was doing more harm than good and alum addition was terminated. Although never fully understood, it appears that breakthrough of lake water turbidity had little effect on GS process foaming but compensating changes in alum dose rate led to breakthrough of alum floc from the sand filters and this did seem to affect foaming. It should be noted that GS process water treatment requirements are entirely dependent upon local feedwater conditions and the experience at BHWP is not necessarily applicable to other sites.

Feed rate to the enriching units was limited by flashing of effluent water downstream of control valves from the effluent strippers. This partially vapourized water caused a high pressure drop in the piping and vibrations in heat exchangers. In 1975, quench water was added to the effluent stream to prevent flashing and feed rates could then be raised so that extraction reached 104% design and the demonstrated capacity was set at 50 kg/h.[37]

In 1976, process conditions were optimized by application of the results of

computer simulation studies and plant trials with respect to the adjustment of operating temperatures. These improvements allowed extraction to increase to 110% design and in 1978 the plant demonstrated capacity was revised to 105.6 kg/h. This extraction rate was achieved at 120% design feed rates and 91% of design depletion. In other words the BHWP-A was being operated at very high feed rates which more than compensated for not achieving the design mass transfer tray efficiency in the extraction and enriching towers.

Performance at this level of 110% design extraction has been maintained since 1978 and development work is continuing to improve tray efficiency by the use of different antifoams and further tray design modifications.

In the first five years of operation of the BHWP-A plant there were few major equipment problems and this fact contributed to the relatively high capacity factors that were demonstrated during the period.[41]

Construction of BHWP-B, comprising units E3 and E4, was committed in 1973 June and construction turn-overs began in 1977 with the new BHWP-B water distillation unit, F2, starting production, on feed from BHWP-A, in the Spring of 1977. The units of BHWP-B incorporate many improvements learned from the operation of BHWP-A,[38] including additional trays to compensate for lower design tray efficiencies. Prior to initial start-up in 1979, the internal surfaces of both units were subjected to a pre-conditioning procedure to ensure that the carbon steel surfaces were protected by the most stable and adherent form of iron sulphide to reduce corrosion and the movement of corrosion products.

This pre-treatment procedure was a result of intensive research on the structure of iron sulphides, and the mechanisms of iron transport [32]. Iron sulphide deposition problems in BHWP-A, although not as severe as those encountered during the early operation of Port Hawkesbury, had resulted in extensions to planned unit shutdowns for tray cleaning as well as efficiency losses during operation. Inspection of towers during the 1980 shutdown showed that pre-conditioning had been successful. The predominant iron sulphide scales were protective pyrite, marcasite and pyrhotite. Deposition on hot tower and dehumidifier trays was minimal and no tray cleaning was required.

Hydrogen sulphide was initially charged to unit E4 of BHWP-B in 1978 September but one month later a crack on an expansion joint bellows, in one of the large diameter gas recirculation lines, prevented continued operation. This and subsequent expansion joint problems resulted in only limited production (52 Mg) from BHWP-B in 1979 and 1980. The majority of the expansion joint problems were caused by hydrogen sulphide stress corrosion cracking of sensitized areas in nickel alloys. These expansion joints have now been replaced with expansion loops in the vertical section of the gas lines.

During the 1980 shutdown to replace the expansion joints, severe hydrogen blistering was found in a number of vessels in BHWP-B. The absorber and

purge towers in units E3 and E4 have been replaced. The selection of steel for these replacement vessels was based on research on corrosion and hydrogen blistering carried out by Ontario Hydro Research.

At the end of 1980 the startup of BHWP-B was well behind schedule but resumed operation is expected in early 1981.

5.3 Glace Bay Heavy Water Plant

The original DCL plant at Glace Bay was to have used sea water as feed and for cooling. The attraction of sea water was its higher deuterium content of 156 ppm versus a maximum of 151 ppm in fresh water. Although the plant was designed to exclude sea water from all but certain areas, the fact that stagnant sea water is extremely corrosive was overlooked during one of the prolonged shutdowns in the commissioning period and caused the destruction of many heat exchanger bundles. When the plant design was reviewed prior to rebuilding, it was found that several other design features, such as the sieve trays and the use of the GS process in fourth and fifth stages, would have made the plant very difficult to operate.

Various schemes were suggested for rebuilding the plant after the original failure and the one finally adopted was proposed by V.R. Thayer who had acted as a consultant to CGE after many years experience with the Dana and Savannah River plants. This scheme made use of the existing tower shells and held promise of producing close to 400 Mg/a D_2O by means of an ingenious variation of the conventional GS process flowsheet.

The Glace Bay plant consists of two separate 200 Mg/a units, each comprising first and second stages, which are known as the "North" and "South" plants. Both these units are connected to a single third stage unit and a water distillation unit which are physically located with the North plant equipment. A schematic flowsheet, Fig. 5 , shows the inter-connections between stages and units. Each unit has two first stage towers and a combined first/second stage tower group. In the event of a first/second stage shutdown, the first stage towers of that unit can be cross-connected to the operating first/second stage tower of the other unit. Both first/second stage towers are connected to the third stage which has its own gas recirculation blower and, unlike the LCCL plants, can operate independently of the rest of the plant, with the penalty of a small loss of heat economy.

In view of the poor experience with sea water feed, the new plant was supplied with fresh water from a reservoir created by damming a local river. The engineering, procurement and construction of the rehabilitated plant was carried out by Canatom MonMax (now Canatom MHG) on behalf of AECL and details of this re-construction project are well documented in previous papers[18] [13]. Major construction was completed, and commissioning was started in 1975[28] with operation of the DW finishing unit on intermediate (20%) product from the Bruce Heavy Water Plant. Hydrogen sulphide gas was charged to half of the plant in 1976 March and extraction of deuterium commenced shortly afterwards. Initial performance of the plant was disappointing due to several equipment failures, partly as a consequence of re-using some material from the original DCL plant and also

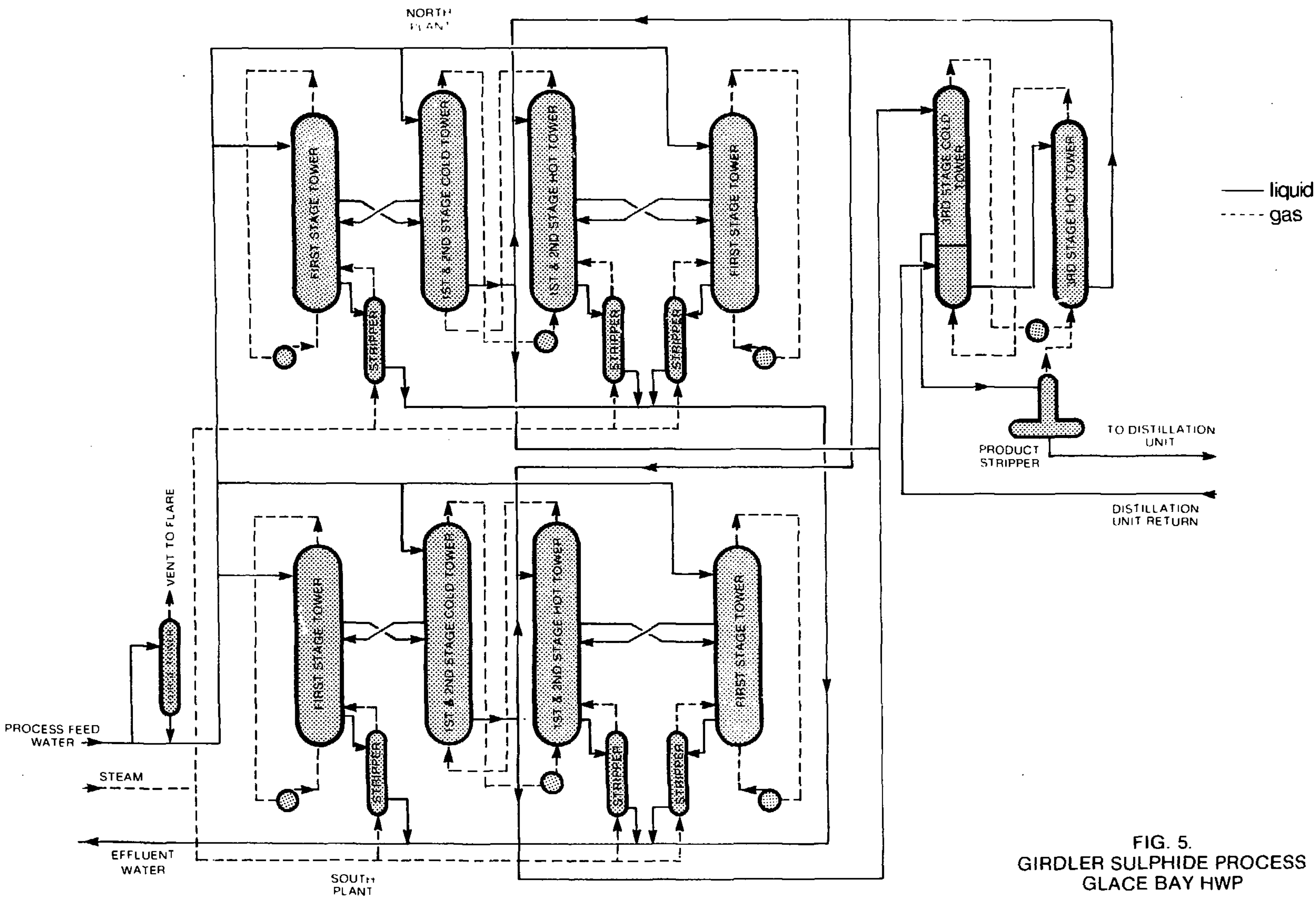


FIG. 5.
GIRDLER SULPHIDE PROCESS
GLACE BAY HWP

due to unfamiliarity with the complexity of the new flowsheet.[30] [31] The first major problem was the observation that sieve tray efficiency was very much less than had been assumed in the re-design of the plant. This was not altogether unexpected because similar, but less serious, observations had been made at both Port Hawkesbury and Bruce. An exact determination of the tray efficiency was made difficult by the occurrence of severe foaming problems in the first stage cold towers. The plant was originally run without using antifoam because of concern about undesirable side effects. However, continued operation in this mode was impossible and antifoam was added starting in 1976.

In early 1977, several heat exchanger shells in the North plant were holed through or severely damaged by erosion/corrosion from water containing hydrogen sulphide. Most heat exchangers at the Glace Bay plant were rehabilitated units from the DCL plant, or new units built to a similar design, and were a unique design to GS process service in that they were 2-pass on both shell and tube-sides. The horizontal pass partition plates in the bundles did not have a tight seal where they were in contact with the shell wall and consequently sour water could leak past them in certain locations. The differential pressure was sufficient to give liquid velocities that caused erosion/corrosion in the vicinity of the seal contact area. These failures were general and progressive in all exchangers handling sour water on the shell side and caused a complete shutdown of the North plant in 1977 March and the South plant in 1977 August.

Whilst the plant was shutdown for repair of the heat exchangers the opportunity was taken to modify the sieve trays in one first stage tower and the two third stage towers, in an attempt to improve tray efficiency. The modification to the third stage sieve trays, which operate with relatively low liquid and gas loadings, was very successful and close to design efficiency was attained. The first stage sieve tray modification produced a small, but somewhat indeterminate, improvement because there were still problems with foaming in the cold tower sections.

Operation with a silicone based antifoam, in the months preceding the 1977 shutdown, produced some undesired experiences due to the accumulation of antifoam additives and degradation products which were, by themselves, foam promoting agents. Although the antifoam was initially effective, the overall performance was poor in comparison to operation at the other plants. When the whole plant was restarted in 1978, no antifoam was added initially but it was very difficult to achieve stable operation at design flows and after a few months one particular first stage tower was unstable at flows in excess of 60% design. With attention focussed on antifoam performance, the R & D program at CRNL identified an alternative silicone based antifoam, which had no foam promoting additives, and trials were conducted at all plants. This antifoam has proved successful at Port Hawkesbury and BHWP until quite recently, when a change was made on the basis of cost rather than performance. Unfortunately, this antifoam did not work so well at Glace Bay, due to the unique process conditions and flowsheet arrangement, and further antifoam changes were necessary.

Despite the antifoam problems, by mid-1978 much more stable and reliable operation was attained at Glace Bay, at flow rates close to design conditions, and this enabled more accurate determinations to be made of tray efficiencies which confirmed that they were indeed quite low. The tray development R & D program at CRNL was by now well underway, the impetus being provided by the problems at Glace Bay and related, but less severe, hydraulic and efficiency problems at the other plants. CRNL suggested that a significant efficiency gain might be obtained by completely re-traying the hot tower sections of the first stage towers and hydraulic stability might be improved by modifying trays in the dehumidification sections. It was decided to try out these changes in the same tower that was modified in 1977, because this particular tower possesses additional instrumentation for performance diagnosis. This was done in 1979 May. This modification was very successful, yielding a substantial increase in efficiency and an improvement in hydraulic stability, with the result that similar changes have now been made to a second first stage tower and it is planned that others will be similarly modified.

Since 1979 the Glace Bay plant has attained a steady level of operation and a very high on-stream capability due to the modular nature of the flowsheet. Although the flowsheet complexity initially presented control problems, these have now been overcome through operating experience and the plant has proved to be controllable by normal GS process techniques.

The water treatment and steam supply systems at Glace Bay have not presented any major operating problems and their reliability has been higher than expected. The DW finishing unit, like that at Port Hawkesbury, has been a source of incapability due to difficulty in preventing and removing surface contamination of the tower packing. To compensate for this deficiency, product is withdrawn at below reactor grade deuterium concentration and upgraded elsewhere.

6. ENGINEERING AND PROCESS DEVELOPMENT

In the 1970-1980 period most development activities were associated with the resolution of process problems because mechanical equipment performance was generally very good. Valves, rotating equipment and instrumentation have performed with a reliability that is better than or equal to typical performance in the petrochemical industry. Analysis of maintenance history data has shown that heat exchangers rank high as a cause of lost production because of the time required to disassemble, repair and re-install. However, plant shutdowns are more likely to be caused by faults in compressors, process pumps or isolation valves.

In the preceding section, reference was made to several problems that were common to most plants and more details of their solution are given in the companion report[17] on R & D activities. The following sections will amplify some of the aspects of these problems, and solutions, that directly affected the operating plants.

6.1 Water Treatment and Process Chemistry

Before Canada embarked on heavy water production by the GS process it was well known from experience at Savannah River that adequate water treatment was essential for stable operation of the sieve trays. Prior to construction, tests were conducted, at cold tower conditions, on the lake water that would be used to feed the Port Hawkesbury plant and it was found that batch samples of water were not especially foamy. Subsequent operation of the completed plant showed that these tests were unrepresentative with respect to water quality and test rig geometry and a more elaborate water treatment system had to be installed to remove dissolved iron and to reduce the foaming tendency of the feed water.

During the last ten years, considerable research was undertaken to try to isolate the impurities in water that exacerbated the natural foaminess of the hydrogen sulphide - water system, and many compounds were identified. It is now generally thought that naturally occurring organics, such as lignins and fatty acids, are the chief culprits and these can be reduced significantly by absorption on activated carbon or by alum clarification. However, the latter operation can produce further problems if it is not properly controlled because the breakthrough of colloidal aluminum also appears to promote foaming. Absorption on activated carbon is expensive and cannot be justified economically. The Nova Scotia plants must clarify to remove iron but this is not necessary at Bruce because Lake Huron has a very low dissolved iron content. All plants now rely on the addition of various types of antifoam compounds to control foaming and by careful analysis of impurity accumulation at critical flowsheet locations.

Another aspect of process chemistry that has received much attention has been the mechanism of iron transport throughout the GS process systems. In addition to the gross deposition of iron sulphide that occurs when soluble iron is not removed from the feedwater, there have been numerous instances of iron sulphide fouling of trays and heat exchangers due to other mechanisms. An extensive R & D program [17] showed [32] that iron transport was largely dependent

upon the type of iron sulphide that was formed in the system and that measures could be taken to promote the formation of species, such as pyrite, that are both adherent and of low solubility. The control of iron sulphide transport and deposition was also found to be linked to the presence of hydrogen gas and sulphur formation. The latter phenomenon, due primarily to ingress of oxygen with the feedwater, has caused problems with blockage of equipment, but at different locations in the various plants. The formation of sulphur is now largely predictable and plant modifications prevent any serious production limitations.

6.2 Materials of Construction

The GS process plants are built of carbon steel components whenever possible in order to minimize capital cost and stainless steels are only used when service conditions would erode the protective iron sulphide layer from carbon steel. The first major materials problems arose through the use of unsuitable grades of stainless steel in heat exchanger tubing where under-deposit pitting caused failures. Some exchanger bundles at all plants have had to be rebuilt with tubes made of more resistant grades of stainless steel and failures from pitting are now comparatively rare.

The general use of carbon steel has presented few major problems when quality assurance specifications for materials and welding procedures were rigidly followed. The incipient failures that have been detected were due to incorrect welding procedures causing sensitization, hydrogen gas build-up in laminations and use of materials outside the specified hardness limits. There have also been instances where carbon steel piping has had to be replaced by stainless steel when erosion/corrosion occurred due to unexpected turbulence.

With the exception of the early problems with pitting, experience with stainless steels has been good, although the circumstances under which they can be used are somewhat limited because it is not permissible to weld stainless steel to carbon steel in GS process service. To overcome this restriction, the use of Inconel alloys has been successfully demonstrated where erosion/corrosion resistance is necessary and welding is unavoidable. The only other materials which are in contact with the hydrogen sulphide-water system are various plastics and resins that are used as sealing materials, such as O-rings in instrumentation. Satisfactory materials were found as a result of testing, under process conditions, in special circulating loops at CRNL.

6.3 Heat Exchangers

Next to the exchange towers, heat exchangers probably represent the next largest capital investment in a GS process plant and their performance has a very significant effect on production costs through heat economy. When only one process stream contains hydrogen sulphide, that stream is usually routed through the tube side to eliminate erosion/corrosion of shell side materials and this also limits the deposition of iron sulphides to a region from which they are removable by hydro-jetting. In the Port Hawkesbury and Bruce plants, conventional single pass exchangers are used, with tubes set on a square pitch in the bundles, but the Glace Bay exchangers are mostly two-pass, on both shell

and tube sides and have tubes set on a triangular pitch. This two pass design does require shell side protection to prevent the erosion/corrosion that occurred at Glace Bay but has the advantage that all piping connections are at one end of the shell, thus reducing the length of pipe runs between shells and other parts of the GS units.

Heat exchangers will operate for 2-3 years without need of a shutdown for cleaning, provided that process chemistry conditions are carefully controlled. Cleaning is usually performed by using high pressure water jets on both shell and tube sides, although this is difficult on the shell side of the triangular pitch bundles at Glace Bay. Some heat exchangers are cleaned in situ by circulation of proprietary chemical cleaning agents, particularly when there is cooling water service on the shell side.

Heat exchanger tube failures can easily be detected by monitoring for hydrogen-sulphide when the lower pressure fluid is normally free of hydrogen sulphide. Leaks in process/process heat exchangers are sometimes detectable by measurement of deuterium concentrations at inlet and outlet. The most common cause of heat exchanger tube failure was originally pitting but since this has been essentially eliminated by the correct choice of materials, the more recent failures are occurring as a result of flow induced fretting. Most GS process heat exchangers are about 12 m long and unsupported tube runs near inlet or outlet nozzles are prone to vibration. Considerable use of computer analysis techniques by CRNL has helped to diagnose and redesign bundles where failures of this type have occurred.

6.4 Sieve Tray Hydraulics

This topic will be dealt with in more detail in the accompanying paper on GS process R & D activities[17], but some comment is necessary here because hydraulic stability of sieve trays is crucial to GS plant performance and historically it has been the most serious cause of lost production. Sieve trays, as replacements for bubble cap trays, were successfully demonstrated at the Savannah River Plant prior to the construction of the Canadian GS plants, but these SRP trays were single pass and only 3.7 m diameter. The larger Canadian plants required trays up to 8.5 m diameter, necessitating a two-pass design, and there was a powerful incentive to minimize tray spacing in the very large towers. Sieve tray design experience, apart from SRP, was limited to hydrocarbon and air liquefaction experience, where the fluid physical properties were very different from the hydrogen sulphide-water system. In the GS process application the unpredictable foaminess of the system caused design difficulties and manufacturers, with the concurrence of the plant operators, chose to assume that the systems were either non-foamy or could be made non-foamy by the use of antifoams and high quality feedwater treatment. The assumption of high froth densities (low foaming tendency) led to the provision of relatively high weir heights to obtain sufficient gas-liquid contact time for deuterium exchange. Non-foamy conditions were impossible to attain and a succession of tray modifications were made at Port Hawkesbury and BHWP-A before suitable combinations of weir height, total hole area and hole diameter were arrived at and stability was achieved. This tray development program was heavily supported by the R&D activities at CRNL, including extensive pilot plant tests of tray performance and measurement of froth heights and densities in the

operating towers by means of gamma ray attenuation [29].

At the Glace Bay plant, tray design was complicated by the need to use the existing tray support rings from the original DCL plant which were set at a closer spacing than had been used elsewhere. Combined with a requirement to handle relatively high F-factors, and the knowledge that there were tray performance difficulties at Port Hawkesbury and BHWP-A the Glace Bay tray design tended to be conservative. The trays had relatively low weirs and a consequent loss of exchange efficiency, particularly the multi-pass hot tower trays, but problems with foaming causing instability were not eliminated.

At Glace Bay, hydraulic instabilities appeared at an unexpected location in the dehumidification sections because the trays in this area were now the most highly loaded trays in the plant and the unique flowsheet arrangement caused foam promoting impurities to accumulate in this region. Since 1978, tray design modifications at Glace Bay have successfully increased tray efficiency and made the dehumidifier trays more tolerant to foaming conditions.

Some mechanical problems were encountered due to the methods by which the large tray decks were supported and restrained, but most incidents involving tray damage were caused by operating errors rather than mechanical faults.
GS process tray design is now very well understood and new plants could be built with a high degree of assurance that the trays will be both hydraulically stable and have an acceptable exchange efficiency.

6.5 Sieve Tray Efficiency

The Savannah River and Dana plants in the U.S.A. were over-designed with respect to the efficiency assumed for their bubble cap trays and consequently the plants had no difficulty in attaining the designed degree of enrichment and product recovery, once hydraulic stability was obtained. In 1961 some tests on sieve and bubble cap trays at Dana were reported which gave deuterium exchange efficiencies of the order of 65 to 70% and, when the time came to design trays for the Canadian plants, it was assumed that these efficiencies would be achievable. The precaution was also taken to check these measured efficiencies against various standard correlations, typical of the hydrocarbon distillation industry, and on this basis the reported efficiencies appeared to be entirely reasonable. It should be noted at this point that the tray development work at CRNL has subsequently shown that correlations such as those published by A.I.Ch.E. are quite inappropriate to GS process conditions. It was also discovered at a later date that the method of analysis used to predict efficiencies from the Dana operation was extremely sensitive to the accuracy of deuterium analyses and the measurement of relatively small flow changes, thus casting doubt on the accuracy of this published data.

Early operation of the Port Hawkesbury plant was plagued by hydraulic stability problems, and operation at flow rates and pressures well away from design conditions, and so any deficiencies in tray efficiency were not readily apparent. It was not until relatively stable hydraulic conditions had been achieved at BHWP-A in 1973 that lower than expected tray efficiencies were suspected and eventually confirmed by 1975. When the Glace Bay plant commenced operation in 1976 it was not altogether unexpected that the tray efficiencies would be even lower than BHWP-A and Port Hawkesbury due to the deliberately

lower weir heights and the use of multi-pass trays. By 1975, pilot plant tests at CRNL had also demonstrated conclusively that tray efficiencies would be lower than design assumptions, with the deficiency being particularly apparent at cold tower conditions.

Optimum GS process tray efficiency is attainable by operation in a narrow stable band just short of hydraulic flooding and also by ensuring that maximum advantage is taken from the enhancement factors attainable from long flow path lengths, devoid of retrograde flow patterns. This latter condition is thought to be more readily achieved with single pass trays, as used at Dana and SRP, than with the multi-pass trays used in some large diameter towers.
The loss of expected tray efficiency had a more serious effect on production capability at Glace Bay than at BHWP-A or Port Hawkesbury because of flowsheet differences. When designing a GS process plant for a specific production rate, a choice can be made between selecting a specified recovery close to the theoretical maximum or relaxing the recovery at the expense of handling more feedwater. The latter choice was selected for Glace Bay, in order to fit the existing configuration of tower shells, and unfortunately this option is more critically dependent upon provision of an adequate number of theoretical plates for design enrichment.

All the Canadian plants have been able to modify their tray designs to increase tray efficiency, although sometimes the required changes have been in conflict with those required to obtain hydraulic stability. No plants have achieved the efficiencies reported from Dana but this has not imposed a severe penalty on the Port Hawkesbury and BHWP-A plants because they have been able to compensate by operation in excess of design flow rates. At Glace Bay it will be possible to restore much of the lost tray efficiency when all of the tower systems are modified in a similar manner to the two towers that have been successfully changed so far. Glace Bay may not have the option to operate so far in excess of design flows as the other plants but the compensating factor will be the high on-stream capability that is achievable with this particular flowsheet arrangement (see Section 7.1).

6.6 Process Control and Analysis

Control of the GS process is achieved by ensuring that all liquid and gas flows through the exchange towers are held at a fixed ratio with an accuracy of about 0.5% This level of precision is unattainable with normal flow measurement and control instrumentation, especially at the large flow rates characteristic of GS process plants. This problem is overcome by using changes in deuterium concentrations, at certain locations in the plant, to indicate off-optimum settings of flow rates. The GS process, and bithermal exchange processes in general, characteristically have concentration profiles that are extremely sensitive to flow perturbations. The success of this method depends upon extremely stable flow control, minimization of inventory changes and being able to take representative samples and accurately analyze their deuterium content. This represents a considerable work load at the operating plants and some attempts were made to automate the collection and analysis of samples. This approach was ultimately successful but, in the case of samples containing hydrogen sulphide, has been abandoned because maintenance requirements for the automatic purification of samples were high and showed no economic advantage

over manual methods. Currently all plants depend for their control on operators manually collecting samples from points within the plant and delivering them to a central laboratory, usually on a once per shift frequency. Some automatic equipment is used to analyze for deuterium in pure liquid streams, such as D_2O in the finishing units, and also for monitoring for hydrogen sulphide leakage into cooling water and effluent streams.

When accurate analyses have been obtained, they have to be interpreted and translated into control changes, if these are indicated. This is not difficult in a simple GS flowsheet, but the logic becomes quite complicated in the case of a flowsheet of the type used at Glace Bay. In this application, control logic was partially developed by use of a computer simulation program written at CRNL. This simulation program, versions of which exist for all Canadian plants, is able to model the results of choosing virtually any set of possible operating conditions, and has been extensively checked against actual plant operating data. Although not directly available to plant control room operators, the program can be used by the plant technical departments to predict the effect of changing certain operating parameters. The program has proved very useful for preparing control strategies, as at Glace Bay, and for determining the most economic set of operating conditions when certain restrictions, such as steam supply or cooling water temperature, are in force.

All the Canadian GS process plants have conventional instrumentation and control systems with no direct computer control of any functions. This arrangement is satisfactory because the plants are generally very slow in responding to a flow change due to the very large inventory of material in the towers and heat exchanger circuits. Under normal operation, corrective flow changes are only made once per 24 hour period and are based on the trend indicated by the preceding three sets of deuterium analysis results obtained at 8 hour intervals.In the case of heat recovery loops, where there could be fluctuations in steam supply temperature or cooling water temperature, changes might be made more frequently. In this latter application, consideration is being given to the installation of distributed micro-processor control systems for improved temperature control, especially in start-up situations.

Data logging computers are used at the GS production plants and the most elaborate installation is at Glace Bay[39] where almost all instrument signals are logged and stored on local discs for at least 24 hours. A condensed version of this data, one minute and one hour averages, is transferred to AECL's central computing facilities at CRNL. This data logging system, known as HEWAC, has proved invaluable for diagnostic purposes and has the capability of recalling and displaying data as tables, schematics or graphs. When unusual incidents have occurred, such as tray flooding, it has been possible to deduce from the graphical displays where the incident originated. In the control room, all alarm signals are logged by HEWAC and this facilitates tracing the origin of faults when several alarms are actuated in close succession. The control room operators also make use of various status displays available from HEWAC but the availability of HEWAC is not essential for safe operation of the plant because all essential information is displayed on the conventional control panel. HEWAC has never been used in a control function and was not intended for this purpose[40]. The system has limited computational capability but this is sufficient for conversion of analog instrument signals to

engineering (SI) units; calculation of certain control functions such as liquid to gas flow ratios, corrected for temperature and pressure; and preparation of summary reports and inventory estimates. The tapes that are sent to CRNL can be searched for data retrieval and analyses over long time periods for the calculation of performance trends.

There is no direct link between HEWAC, or any of the other site data loggers, and the computer simulation program referred to earlier but this simulation is accessible via remote terminals at all plant sites.

6.7 Product Finishing

The GS process is only used to produce D_2O at 10 to 25% enrichment, depending upon initial design assumptions and local plant operating conditions. Final upgrading to reactor grade heavy water, 99.75% D_2O, was intended to be carried out by distillation of heavy water followed by treatment to remove impurities. This route is followed at the Bruce plant but operating difficulties at the AECL plants at Port Hawkesbury and Glace Bay have made it economically attractive for product to be withdrawn at about 94% D_2O and this water is then sent to AECL's facility at CRNL for final upgrading by electrolysis.

Distillation of heavy water requires a very large number of theoretical plates because the relative volatility is only about 1.05 at economic operating conditions. At the Bruce-A plant a conventional sieve tray plant was selected for this distillation operation and this has proved to be a reliable and rugged process with no stringent feed water pre-treatment requirements. The only significant modification made to this installation was the removal of outlet weirs from the sieve trays in order to reduce pressure drop and improve overall efficiency. The principal disadvantage of using conventional sieve trays is that the plant volume is relatively large and thus contains several months' inventory of heavy water.

At the Port Hawkesbury plant a high performance distillation packing was chosen in order to minimize inventory. This packing, made of phosphor bronze with an oxidized surface, works extremely well if the system can be kept clean and this requires careful treatment of the intermediate product from the GS plant. Hydrogen sulphide is removed from GS product by conventional steam stripping and the water is further purified by one or two steps of evaporation after being dosed with potassium permanganate to remove organics. This pre-treatment operation has not been sufficient to prevent gradual fouling and surface deterioration of the high performance packing.

Experience at the Glace Bay plant has been somewhat similar, although initially the first water distillation column at Glace Bay was packed with plastic pall rings, which had an unacceptably high pressure drop, and organic matter leached from the packing fouled the downstream column. In 1977 the plastic pall rings were replaced by proprietary phosphor bronze rings, which solved the pressure drop problem, but soon suffered from surface contamination and deterioration of the oxide coating.

Development work at the operating plants and at CRNL has devised a feed pre-treatment system that should protect phosphor bronze packings from fouling

and deterioration but the availability of the CRNL electrolysis plant has made the installation of this system uneconomic at present.

BHWP-B also utilizes a high performance packing for water distillation. It has been concluded that the savings due to reduced inventory and lower steam requirements more than compensate for the higher initial cost and extensive feed treatment requirements. The feed treatment system at BHWP-B comprises oil separation, permanganate addition and two stages of evaporation in order to ensure clean feed. This system has operated successfully since 1976 with no apparent deterioration of the phosphor bronze packing.

6.8 Energy Supply

GS process heavy water plants are intensive consumers of energy, primarily in the form of steam for heating water and hydrogen sulphide gas to hot tower operating conditions. The required energy input is typically 10,000 Mg of steam per Mg heavy water produced, when steam condensate is recycled.

6.8.1 Port Hawkesbury

Steam for this plant is supplied by back-pressure turbines at the 75 MWe oil-fired Point Tupper-1 generating station of the Nova Scotia Power Corporation (NSPC). The power station is located about 1000 m from the heavy water plant where the steam is used indirectly in heaters on the humidification circuits and condensate is returned to the power plant. The heavy water plant in essence acts as a condenser for the generating station and, to fulfill this role during GS plant outages, parallel heat exchangers supplied with cooling water are provided in the GS plant. Reliability of the steam supply has been generally satisfactory in recent years with the exception of the steam supply line failure referred to earlier and the fact that there is only 25% redundancy in the system. Limited additional steam is available via a tie line to the adjacent 150 MWe Point Tupper-2 station.

The recent announcement by the Federal Government in Canada that Port Hawkesbury is being recommended as the site of the pre-feasibility study of the fluidized bed combustion of Cape Breton coal is encouraging because steam from oil-fired boilers is becoming very expensive. Ultimate conversion of the Point Tupper plant to coal firing would maintain Port Hawkesbury's energy costs in line with those pertaining at Glace Bay.

At typical operating conditions the Port Hawkesbury plant consumes 24.0 MWe as electrical power and 130 kg/s cf steam at 200°C and 1275 kPa. With allowance for condensate return, total energy consumption is in the range of 25 to 30 GJ/kg D_2O on an instantaneous production basis.

6.8.2 Bruce

A major reason for locating heavy water plants at the Bruce Nuclear Power Development was the availability of steam at an attractive cost. Nuclear steam is considerably less expensive than steam generated from gas, oil or coal fired boilers.

BHWP-A was designed to be supplied by steam from a medium pressure steam generator which in turn was supplied by higher pressure steam from the secondary circuit of the 200 MWe Douglas Point Nuclear Generating Station (DPGS) or an auxiliary oil fired boiler plant. This system functioned very well and steam from DPGS was always used in preference to that from the oil fired boilers to minimize operating costs. Operation with the load shared between both sources was a common mode and provided a high degree of reliability.

When the four units of the Bruce Nuclear Generating Station were built, they were each designed to generate 750 MWe plus the thermal equivalent of 100 MWe as additional steam for the Bruce heavy water plants A,B and D. When these units came into operation from 1976 onwards, almost all steam supplied to the heavy water plants was generated by the five nuclear power reactors and the oil fired boilers ceased to be used on a regular basis. Steam and electricity consumption, per unit of heavy water produced, is comparable to the figures given for Port Hawkesbury.

The steam supply system of the Bruce Nuclear Power Development (BNPD) is an outstanding example of the successful application of nuclear power to a chemical process industry[25]. Studies are underway to extend the use of this steam supply to other energy intensive industries to be located adjacent to BNPD.

6.8.3 Glace Bay

This plant uses the direct injection of high pressure steam for effluent stripping and the supply of heat to the hot tower sections and consequently there is no return of condensate to the supplier. High pressure steam is supplied from the NSPC Seaboard Power Station at Glace Bay and is transmitted via a 1.5 km long steam line. There are six coal fired boilers of various capacities at the Seaboard station and this has proven to be a highly reliable source of steam for the heavy water plant. In the event of coal supply interruption, these boilers can be switched to oil firing.

Normal electricity consumption at Glace Bay is 21.5 MWe and the steam supply rate is 96 kg/s at 350°C and 4150 kPa. No condensate is returned and the total energy consumption is in the range of 25 to 30 GJ/kg D_2O on an instantaneous basis.

6.8.4 Waste Heat Utilization

GS process heavy water plants unavoidably discharge large quantities of low-grade heat in their effluent water streams. Depending upon the location, local environmental regulations can require the effluent temperature to be lowered, by dilution with cooler water, before discharge beyond plant boundaries. Several schemes have been proposed to make use of this low grade heat, rather than waste it by dilution, and one project is currently active at Glace Bay. At this site a pilot project will use the warm water for heating a greenhouse complex where it is hoped to grow fresh fruit and vegetables all year round.

7. PRODUCTION CAPABILITY

7.1 Present Status

The annual production achievement of the Canadian GS process heavy water plants from 1970 to 1980 are listed in Table 1, and their nominal design ratings are given in Table 2. As a general rule, for production forecasting, annual production capability is taken as 70% of the design rating. The plants at Port Hawkesbury and Bruce are capable of holding or exceeding their design hourly ratings and in their case the 70% represents time lost for maintenance turnarounds and an allowance for unplanned outages. The design of these plants is such that the loss of more than one of the three parallel first stages in a nominal 400 Mg/a unit will result in the shutdown of the whole unit. In the case of the Glace Bay plant an on-stream capability of better than 90% has been demonstrated for the last 2½ years because production can always be maintained so long as one of the two combined first/second stage towers and the third stage are in operation. Thus the Glace Bay plant can still produce at a reduced rate when four first stage towers and one combined first/second stage tower are out of action, which is an unlikely situation. The principal reason for rating Glace Bay at 70% of nominal is the lower than design tray efficiency and not availability. Further tray modifications at Glace Bay should increase production capability to more than 70% of nominal design.

The LCCL designed plants at Port Hawkesbury and Bruce require maintenance shutdowns for the complete unit at about two year intervals. These planned outages normally last 4 to 6 weeks and are carried out during mild weather conditions to avoid freezing of stagnant lines. Relatively long turnaround periods, in comparison to the petrochemical industry, are necessary because all equipment must be thoroughly purged of hydrogen sulphide before any maintenance can proceed.

The modular design of the Glace Bay plant allows maintenance of most units to be carried out while the remainder of the plant is in operation. A full plant shutdown is only necessary every three or four years for servicing the utility systems or the third stage and water distillation unit.

The production capability of Canadian heavy water plants at the end of 1980 is summarized in Table 2.

7.2 Supply and Demand

At the end of 1980 the Ontario Hydro BHWP plants are fully committed to the supply of heavy water for CANDU reactors under construction in the Province of Ontario. The delayed start up of BHWP-B plant may result in a temporary shortfall in the early 1980's but following this there will be ample capacity to meet Ontario Hydro's requirements until the early 1990's.

The AECL plants at Glace Bay and Port Hawkesbury have met all outstanding commitments and are now stockpiling heavy water in anticipation of off-shore sales in the 1980's.

TABLE 1

CANADIAN HEAVY WATER PRODUCTION FROM 1970 TO 1980

(Megagrams per calendar year)

YEAR	PORT HAWKESBURY	GLACE BAY	BRUCE
1970	13		
1971	63		
1972	183		
1973	129		281
1974	294		640
1975	175		605
1976	112	39	800
1977	225	63	655
1978	282	176	736
1979	242	236	638 (1)
1980	321	249	653 (1)

Note: (1) Includes a contribution from BHWP-B (52 Mg total).

TABLE 2

STATUS OF CANADIAN D_2O PLANTS - 1980 DECEMBER

PLANT	DEMONSTRATED HRLY RATING ($kg\ D_2O/h$)	NOMINAL PLANT SIZE (Mg/a)	COMMENTS
Port Hawkesbury	50.0	400	In operation
Glace Bay	38.0	400	In operation
LaPrade	-	800	Mothballed in 1978
BHWP-A	105.6	800	In operation
BHWP-B	-	800	Commissioning
BHWP-C	-	800	Cancelled 1974
BHWP-D	-	800	Mothballed 1978

7.3 Economics of Heavy Water Production

Canada does not quote a world market price for large lots of heavy water because the price is normally negotiated as part of the total cost of supplying a CANDU nuclear power station. The advertised price for heavy water in the United States in 1980 was $255 CDN/kg ($97 US/lb). It is interesting to note that the original contract for purchase of heavy water by AECL from CGE at Port Hawkesbury was in the range $35 CDN/kg to $45 CDN/kg in 1970, a reflection of the general rate of inflation in the cost of chemical plants and the price of energy over the last decade.

The capital cost of the Port Hawkesbury plant was reported as $70 million in 1970, representing about $175,000 per installed nominal Mg D_2O/a capacity. By 1980, a new GS process production plant in Canada was estimated to cost of the order of $1.2 million CDN per installed nominal Mg D_2O/a.

Heavy water production costs are a function of capital depreciation, maintenance, energy, labour and material supplies but the relative contributions of these elements vary widely at the Canadian plants due to differences in construction dates and the sources of energy.

The inventory of heavy water represents about one third of the capital cost of a CANDU Nuclear Steam Supply System (NSSS) or 15% to 20% of the total capital cost of a CANDU Nuclear Generating Station. There is consequently a very strong incentive to minimize or reduce the cost of heavy water production.

7.4 Manpower Requirements

There are currently about 2200 persons directly employed in the heavy water production plants in Canada, of which about 200 are professionals. In addition to these persons, some plants use contract maintenance personnel during plant turnaround periods.

A very important consideration in the staffing of heavy water plants is the provision of training programs for all personnel to ensure that each position in the plants is filled by a person with appropriate knowledge and skills so that the plants are operated safely, effectively and efficiently. Formal training is provided by lectured courses and demonstrated skills in the classroom and the field. Special emphasis is given to safety related training such as the monthly requalification of personnel required to work in areas where hydrogen sulphide gas might be present.

8. SAFETY AND ENVIRONMENTAL CONSIDERATIONS

8.1 Safety Performance

The most important safety concern in a GS process heavy water plant is the prevention of personnel exposure to hydrogen sulphide gas which is highly toxic and present in large quantities (600 Mg in a typical unit) and at high pressure (2000 kPa). The physiological effects of hydrogen sulphide depend upon the concentration and duration of exposure but can generally be classed as acute or sub-acute.

Acute poisoning is a situation where exposed persons are overcome and require resuscitation, typically indicated by unconsciousness or cessation of respiration. Prolonged exposure or exposure at high concentrations can result in death due to anoxia. The threshold level of acute exposure is between 700 and 1000 mg/m^3 (500-700 mg/kg).

Sub-acute poisoning may occur when concentrations are lower than those which produce acute poisoning and persons exposed to such concentrations, while not requiring resuscitation, do show physiological effects varying in degree from eye irritation, headache, disturbed respiration, dizziness, nausea and vomiting.

Protection against hydrogen sulphide within the plants is provided by:

(a) The application of rigorous standards in terms of material specifications, equipment and design.

(b) Management of the human element by use of procedures, extensive training and personnel safety equipment.

One element of (b) above is the "buddy" system. In areas of the plant where hydrogen sulphide is present workers must carry a breathing air supply and operate in pairs, within sight of each other but not closer than 3 m, so that if one individual is overcome by gas, his buddy can use his escape pack to retreat to an alarm station, summon help, don a rescue pack with full face mask and return to resuscitate his buddy, pending arrival of a rescue team.

The incidence of hydrogen sulphide exposures at the plants, in terms of acute and sub-acute exposures, has been acceptably low. In the period 1970 to 1980 there have been a total of 15 acute exposures and no fatalities. The incidence of sub-acute exposures has been trending downwards over most of this period.

The lost time accident history at the plants has been typical of the chemical process industry. Almost all lost time accidents are the result of common industrial type mishaps, e.g. back injuries from improper lifting techniques, and very few are the result of exposure to hydrogen sulphide. The improving safety records at the plants are attributed to increasing attention to safety programs and training, general training, procedures, maintenance of plant integrity and safety equipment.

8.2 Environmental Performance

Environmental performance is primarily measured in terms of:

a) hydrogen sulphide discharged in the liquid effluent from the plant;

b) hydrogen sulphide discharged to the atmosphere from process equipment leaks and as sulphur dioxide from the hydrogen sulphide burned at the flare stack during controlled or emergency venting.

Hydrogen sulphide in the liquid effluent from a few ug/kg to a few mg/kg can be injurious to some forms of aquatic life. The two Nova Scotia plants discharge liquid effluent to the sea and different regulatory limits apply in this situation than for the discharge to Lake Huron from the BHWP plant. The number of occasions during which the hydrogen sulphide concentration in plant effluents has exceeded regulatory limits has been very low.

Hydrogen sulphide in the atmosphere is readily detected by its distinct odour resembling rotten eggs. The human nose can detect concentrations of 0.02 mg/kg or less which is well below levels of hazard to health of humans. Consequently, the prime indicator of hydrogen sulphide emission to the atmosphere is odour complaints from the public in the surrounding area. The number of odour reports which were confirmed as originating from the Nova Scotia plants has been less than 10 per year. In the case of Port Hawkesbury, the presence of an adjacent pulp mill has caused some confusion over the origin of reported odours. In the early years of operation of BHWP-A more frequent odour reports were received because of incomplete combustion of small H_2S releases to the flare system and the fact that the prevailing wind direction and poor dispersion carried stack effluent over land. The situation has been rectified by adding propane to the flare stack to ensure continuous combustion at the tip and providing an amine scrubbing system to absorb hydrogen sulphide from routine venting operations prior to discharge to the stack.

Protection of the general public around the plants in Nova Scotia is provided by the Gas Dispersion System, described in section 5.1, and measures to divert local traffic. At the BHWP plant there is a 2 km exclusion area which also serves the Bruce nuclear generating stations.

9. FUTURE PROSPECTS

9.1 Production in the 1980's and beyond

The Canadian GS process heavy water plants are expected to remain in operation to near the end of this century. In the short term there will be emphasis on improving the energy efficiency of the production plants, especially in Nova Scotia where steam is supplied from both coal and oil fired power stations. At the BNPD complex in Ontario, the cost of energy will be relatively low and inflation-proof because steam is supplied from the Bruce nuclear generating stations.

When the need for an increase in the rate of heavy water production arises, Ontario Hydro and AECL will be able to respond fairly rapidly by completing construction of the BHWP-D and the La Prade plant.

9.2 Development of the GS Process

The research and development program(33) (34) that has supported the Canadian heavy water production program for the last decade has also brought forward many suggestions for the improvement of future generations of GS process plants. As described in Section 4 , the GS process is constrained by the physical properties of the hydrogen sulphide - water system and there does not appear to be any economic scope for operation at more widely separated temperatures which, if it were possible, would reduce the number of theoretical plates required. It is possible, however, to devise some ingenious variations on the conventional bithermal flowsheet which will increase the recovery of deuterium from a given plant volume. Such variations include the flowsheet now used at Glace Bay, hot feed proposals and other means of conserving feed. In recent years, more attention has been focussed on reducing energy requirements because all the existing plants were designed before the impact of the 1973 oil crisis became apparent. There is some scope for reducing steam requirements through the use of more elaborate heat exchanger networks and improvement in heat transfer tray efficiency, but potential savings are not likely to reduce current energy requirements by more than 10%.

GS process development will continue through the 1980's in the expectation that further improvements can be made to mass transfer tray efficiency, heat transfer tray efficiency, antifoam performance, mechanical equipment performance, etc.

9.3 New Processes

The GS process is expected to be the pre-eminent method of heavy water production until 1990 because there are currently no economically superior large scale processes. However, in order to ensure the supply of the least expensive heavy water, AECL and Ontario Hydro are jointly pursuing research and development programs on alternative processes.(35)

For some years, AECL have worked on the development of the hydrogen-amine exchange process which is attractive as a small production unit, of less than 100 Mg/a, that could be built in conjunction with a world-scale ammonia

synthesis plant. The feed to the hydrogen-amine process would be synthesis gas from the steam reformers from which deuterium can be extracted and then enriched in a bithermal exchange process. Synthesis gas, depleted in deuterium content, would then be returned to the main plant's ammonia synthesis loop. It is possible to design a water feed step for the hydrogen-amine process that would make the process independent of an ammonia plant and allow construction of large scale, 400 Mg/a, units. Current estimates indicate that the cost of this water feed step, undemonstrated in a prototype plant, would not give the water-hydrogen-amine process a significant economic advantage over the GS process. There are no plans to build a hydrogen-amine exchange plant in Canada, but development has reached the stage where a complete design for a 70 Mg/a parasitic unit is available.

A potentially elegant process for the large scale production of heavy water is the bithermal hydrogen-water exchange process using fixed bed catalysts in both cold and hot exchange sections. During the last decade, major advances have been made in the development of suitable catalysts that retain their activity in the presence of liquid water. The attraction of this process is simplicity, a relatively large difference between hot and cold tower separation factors, and the fact that hydrogen is neither toxic nor corrosive. Research and development will continue through the 1980's to commercialize this process which currently appears to be a promising successor to the GS process.

Ontario Hydro and AECL are also participating in fundamental research into Laser Isotope Separation (LIS) processes which have very high separation factors. The economic attractiveness of such processes will depend upon the development of an inexpensive front-end transfer step for exchange of deuterium from water or hydrogen to a chemical compound that will respond to LIS.

10. SUMMARY

During the 1960's and 1970's, the Canadian heavy water program was directed to establishing a reliable and economic source of supply in support of the CANDU reactor program. To satisfy this goal, the Girdler-Sulphide process was adopted in Canada because this process had been well proven in the U.S.A. and was the only one offering the dependability required. Improvement of the GS process and development of new processes is a continuing activity in support of this goal.

The original American heavy water plants were built in 1952 as part of the military program and economic considerations may not have been of prime concern. However, when Canada built its first heavy water plant, economic considerations were of prime importance and this led to very significant differences in the size of the Canadian and American plant's process units.

When Canada committed its first heavy water plant it underestimated the difficulties of developing this industry; the process seemed deceptively simple. Although Canada had chemical process expertise, it did not have any expertise in the GS process and neither did it have any pertinent R & D work in progress. Through a bilateral agreement with the U.S.A. it had relatively free access to GS technology. In spite of this, the development of the Canadian Heavy Water Industry has been difficult, although ultimately successful, as the current performance of Canada's three operating plants attests.

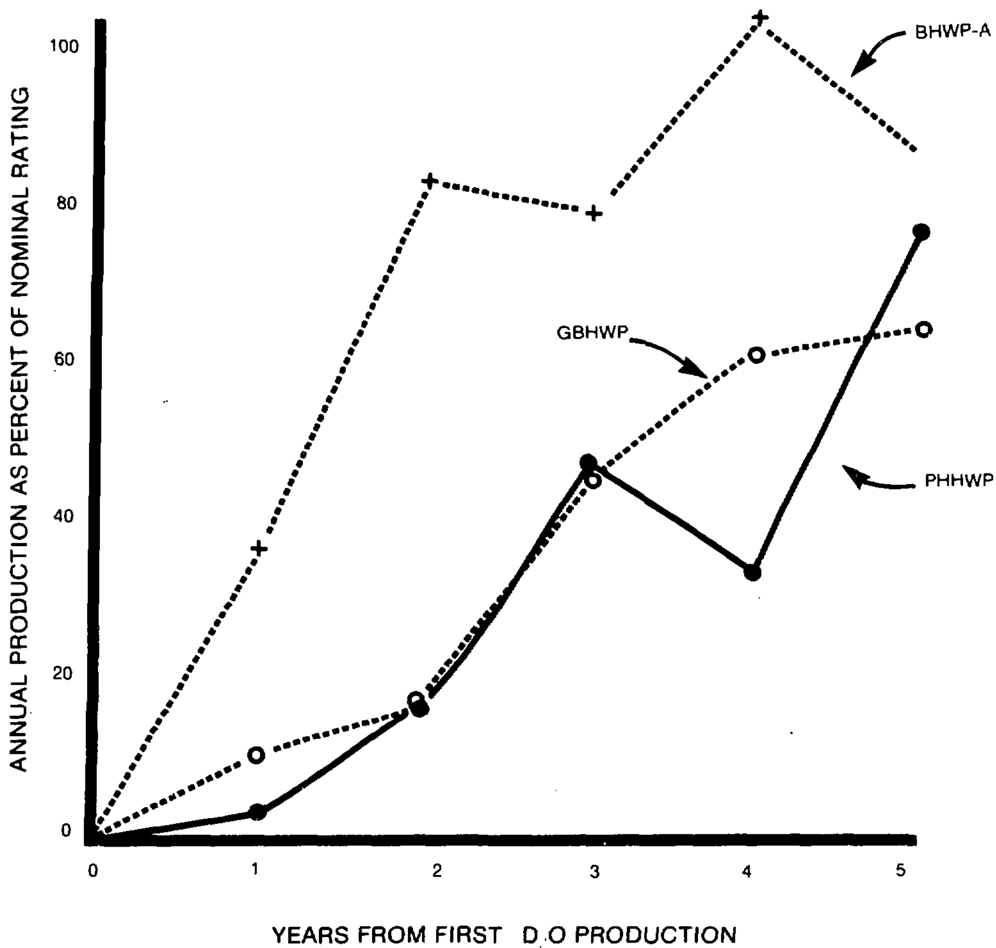
During the early 1970's the Canadian heavy water industry was forced to focus on overcoming operating problems and this was achieved primarily in two ways. First, plant operators and designers were able to learn from their mistakes and generally benefit from increasing experience. Secondly, the industry mounted a large research and development program aimed at developing an improved understanding of the Girdler-Sulphide process, in order to overcome and minimize the problems being encountered and to fine-tune plant operation. The plant operating problems continued for some years and the efforts which eventually were successful in overcoming them have proven the value of experienced plant designers, construction contractors and component suppliers, experienced commissioning and operating staff, and a large, sophisticated and continuing research and development thrust. Success also requires that the work of these functional groups be well integrated, i.e, that there is a close relationship between the users and the creators of technology.

The development program has been staffed by up to 60 scientists and engineers in AECL and Ontario Hydro. In addition, there has been a substantial involvement of plant designers, operators, and manufacturers of plant components, in the development program. The program has been established as an industry-wide effort and owing to the open exchange and cooperation within the industry it has been possible to avoid unnecessary duplication of effort and to benefit from each other's developments. There are now at CRNL about 20 scientists and engineers engaged in R & D in support of the GS process and they are supported by a significant amount of industrial contract research.

This development program has been very successful. One measure of the success of the program and of the general learning experience is obtained by comparing the time to reach high production levels in successive plant units.

In Figure 6, the relatively rapid rise of production levels at BHWP-A is contrasted with the slower rate of rise at Port Hawkesbury. This is an effective demonstration of the fast learning curve at BHWP that resulted from the successful transfer of technology and know-how from the similar design of plant at Port Hawkesbury. The curve for Glace Bay is depressed, relative to BHWP, because the flowsheet and plant design is dissimilar and there were initial problems with heat exchanger reliability and sieve tray efficiency. There was consequently less opportunity at GBHWP to take direct advantage of the experience gained at Port Hawkesbury and BHWP.

Through the optimization of design and operating parameters, some impressive gains have been made in the productivity of the Canadian plants. Figure 7, which is based on Table 1 , shows how the annual production of heavy water in Canada has steadily increased over the last decade and, when BHWP-B is brought into full production, will reach approximately 1850 Mg/a.



ANNUAL PRODUCTION (AS % NOMINAL RATING) FOR
FIRST 5 OPERATING CALENDAR YEARS

+ BRUCE HEAVY WATER PLANT - A
● PORT HAWKESBURY HEAVY WATER PLANT
O GLACE BAY HEAVY WATER PLANT

FIG. 6.

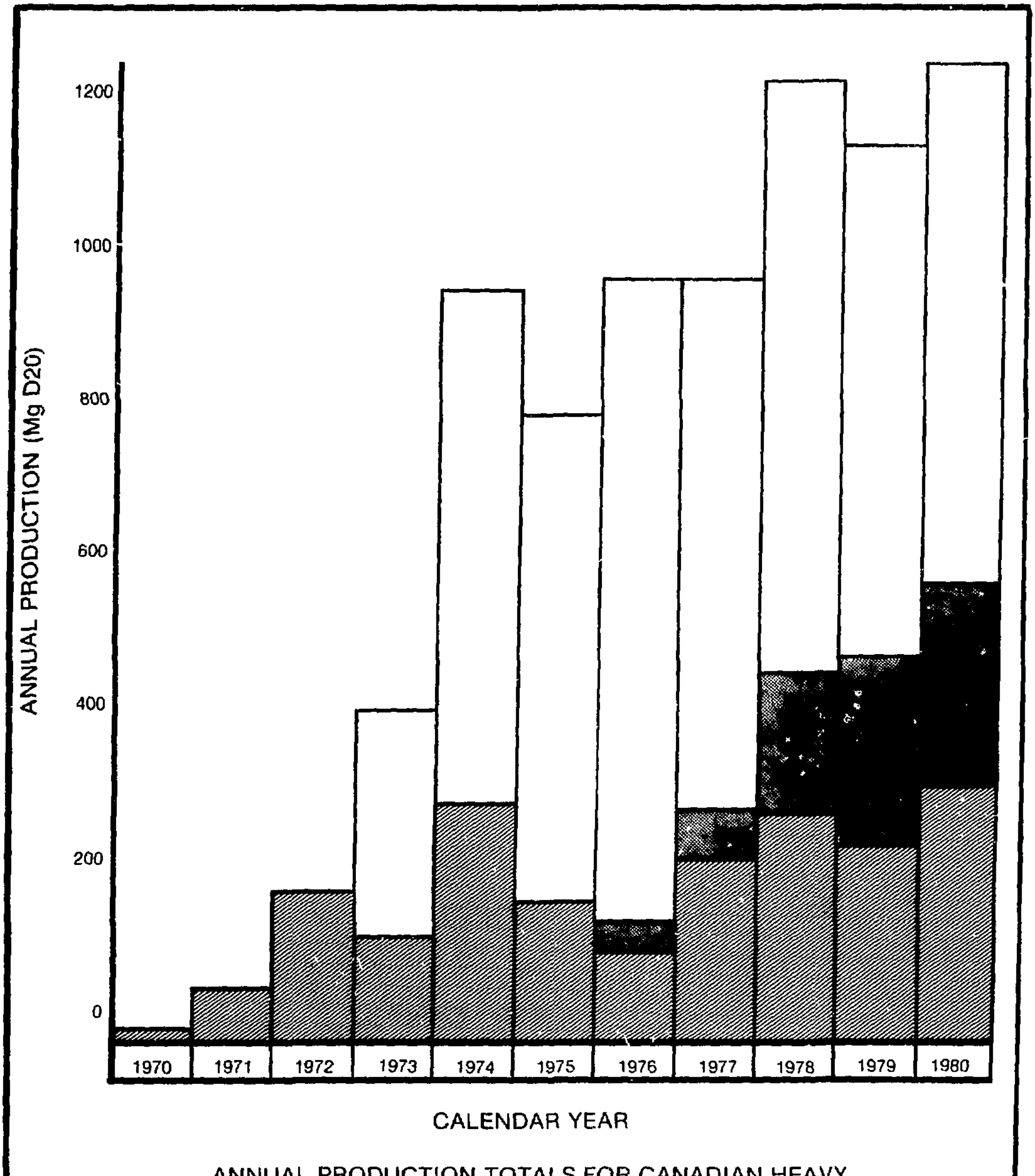

1200
1000
800
600
400
200
0
ANNUAL PRODUCTION (Mg D20)
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
CALENDAR YEAR
ANNUAL PRODUCTION TOTALS FOR CANADIAN HEAVY WATER PLANTS
PORT HAWKESBURY
GLACE BAY
BHWP

FIG. 7.

11. ACKNOWLEDGEMENT

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None of the achievements reported here would have been possible without the dedicated effort of the 2200 persons employed in the heavy water production industry in Canada.

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Heavy Water Production Benefits of a Supporting R&D Program

1. INTRODUCTION - A.R. Bancroft, CRNL

The production of heavy water in Canada to supply CANDU nuclear power reactors began in 1970. The history of the evolution of this new Canadian industry, based on the Girdler-Sulphide (GS) process, is described in a companion report (1.1). Research and development (R&D) activities to support the production plants began while the Port Hawkesbury Heavy Water Plant (PHHWP) was being built, a year or so before the first water was produced. Although problems had not been identified by the plant owner, the Canadian General Electric Company Limited (CGE), it was considered prudent by Atomic Energy of Canada Limited (AECL) and by CGE to begin the building of a technical support capability. This followed the failure of Deuterium of Canada Limited (DCL) to bring the Glace Bay Heavy Water Plant (GBHWP) to production following the 1968 startup attempt. Also because of the DCL failure the construction of a third heavy water plant was committed to satisfy the increasing demand of an expanding nuclear power program. This plant, at the site of Ontario Hydro's Bruce Nuclear Power Development, brought AECL into the picture as plant owner and Ontario Hydro (OH) as operator. These three parties, AECL, CGE and OH, were responsible for establishing and shaping the R&D program that grew to involve a staff of more than 50 engineers and scientists by the mid-70s. Some of the achievements of this program were reported earlier (1.2).

During the design, construction and early operation of the Canadian plants information from the Dana and Savannah River Plants was made available through a United States-Canada technology exchange agreement. Although this technology was initially invaluable it proved to be inadequate to bring the Canadian plants to mature operation. Production at design rates was achieved only after the Canadian program had made significant advances. Some of this technology was generated by the designers and operators and was rapidly incorporated into the plants. Another pool of technology was evolved at the R&D sites. Throughout the entire period considerable effort has gone into the transfer of technology between sites.

There were many lessons learned during the program. One purpose of this report is to alert others considering establishing a heavy water production industry to the benefits of R&D support and to provide some guidance concerning the magnitude required to ensure success. Another purpose is to indicate the broad range of technology generated within the Canadian program that may be of value to others.

2. ORGANIZATION OF R&D EFFORT - A.R. Bancroft, CRNL

2.1 Location of GS Process Effort

As the first step in establishing a technical support team AECL assembled a working group in 1966 to assess the economics of competing processes. This drew from the staff of the Chalk River Nuclear Laboratories (CRNL) and involved individuals from six Canadian chemical and consulting companies. This group and its successors looked at the ammonia-hydrogen exchange process and showed that the amine-hydrogen exchange

process was much more attractive. The advantages were sufficient to establish a permanent heavy water R&D group and begin to develop the amine-hydrogen process (2.1). It was from this base at CRNL that the GS process support team grew to involve more than twenty Canadian establishments. Table 2.1 lists the participating contractors.

Table 2.1

GS PROCESS R&D - CONTRACTORS

Contractor	Location	Typical Contribution
Canadian General Electric	Peterborough	Metallic and other materials
Canatom MHG	Montreal	Physical property evaluation
Dalhousie University	Halifax	Organic impurities in feedwater
Dilworth, Secord, Meagher	Toronto	H_2S release dispersion modelling
General Electric Company	Schenectady	Sieve tray analysis, foaming
Guelph Engineering	Cambridge	Valve development
Hatch Associates	Toronto	Heat exchange system modelling
LaSalle Hydraulics	Montreal	Heat exchanger tube vibration
Lummus Canada	Toronto	Sieve tray development
McGill University	Montreal	H_2S ignition studies
Nova Scotia Research Foundation	Dartmouth	Analytical chemistry, process chemistry, gamma scanning, effluent monitors, leak detectors
Raylo Chemicals	Edmonton	H_2S and antifoam chemistry
Sulfur Research Institute	Calgary	Thermodynamics of metal sulphides
Sulzer Canada	Toronto	Water distillation feed treatment
Union Carbide	Toronto/Tonawanda	Sieve tray development
University of Alberta	Edmonton	Vapour pressure of mercaptans
University of New Brunswick	Fredericton	Corrosion of materials

CGE was the builder and owner until 1975, when it sold the Port Hawkesbury HWP to AECL.
Canatom was designer-constructor of the rehabilitated Glace Bay HWP (1971-1976), and the LaPrade HWP (1974-1978).
Lummus was the designer-constructor of the Port Hawkesbury HWP (for CGE), Bruce A HWP (for AECL, sold to OH in 1973) and Bruce B and D HWPs (for OH).
NSRF has provided continuing R&D and other services starting in 1972.

2.2 Discipline of Effort

During the early years of commissioning and operating it became clear that the effects of the differences in process arrangement and equipment type and size between the US plants built during the 1950's and the Canadian plants were not fully understood. Since the US plants operated reliably at high capacity it was believed that detailed understanding of

these differences was essential to the success of the Canadian production program. R&D effort was applied to short-term problems to satisfy the needs identified by the operators. In addition, topics were identified for which substantial gain was forecast from longer-term work. Those topics that have contirued to receive attention throughout most of the decade are listed in Table 2.2. Also indicated are the sites at which most of the work was done.

Table 2.2

GS PROCESS - DISCIPLINE OF R&D EFFORT

	AECL				OH	
	CRNL	WNRE*	GBHWP PHHWP	CC*	BHWP	OHR*
1. Process Analysis and Control	x		x		x	
2. Process Chemistry	x	x	x		x	
3. Analytical Chemistry	x	x	x		x	x
4. Materials, Corrosion	x	x	x		x	x
5. Mechanical Equipment	x				x	
6. Sieve Tray Hydraulics and Mass Transfer	x		x	x	x	
7. Gamma Scanning	x			x	x	
8. Water Distillation	x			x	x	x

* WNRE - Whiteshell Nuclear Research Establishment, Pinawa, Manitoba
CC - Chemical Company Head Office, Ottawa, Ontario
OHR - Ontario Hydro Research Department, Toronto, Ontario

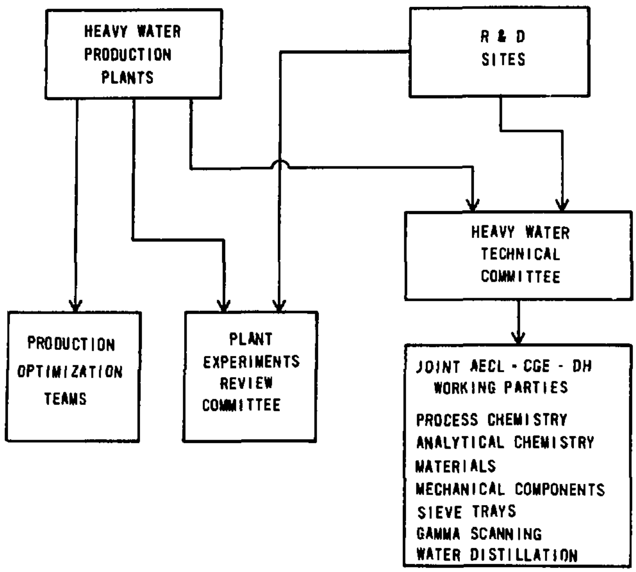
2.3 Co-ordination of Effort

There was sufficient common interest among the three companies that were involved early in the decade (AECL, CGE and OH) that they recognized the benefits that could be gained by sharing experiences. This was as true for process problem-solving as it was for operation and maintenance methods and procedures. The organization for R&D support that was evolved, and remained in effect for much of the decade, is represented in Fig. 2.3. Two committees and two groups of working parties and optimization teams were established under the control of the management of the heavy water production plants and the R&D sites. Not shown in the figure, but vital to the efficient functioning of the activities is the two-way communication at all working levels. A description of each group follows:

Heavy Water Technical Committee

This committee has the senior R&D co-ordinating role. It is composed of the technical managers from all heavy water plants and their

FIGURE 2.3
GS PROCESS R & D - COORDINATION



counterparts from the R&D sites. It meets several times each year to review the activities of the working parties and to ensure that they are consistent with plant problems and management objectives.

Working Parties

These groups are composed of the technical experts from the R&D sites and members of the plant technical departments involved with the relevant projects. The frequency of meeting varies from four times a year during periods of pressing problems to once a year when problems are few. Some of the individuals making up the working parties are also involved in the two following groups.

Production Optimization Teams

Each plant established a team that meets regularly to review plant performance, identify key problems and identify solutions using best available information. Where information is lacking the assistance of the relevant working party is requested. These teams are composed largely of the staff of the plant in question, but they have representatives from the other plants and the R&D sites.

Plant Experiments Review Committee

This committee was established by OH and AECL to conduct in-plant experiments in the Bruce HWP. It plans and co-ordinates experiments that are conducted by the plant operations staff, reviews the results and makes recommendations for plant improvements.

All of these groups have co-ordinating functions only. Responsibility for implementing plant trials or conducting laboratory tests rests with the line management of each site. The system has worked because individuals with appropriate authority have been assigned as members to the various groups and committees.

2.4 Other Heavy Water Processes

It was mentioned in Section 2.1 that the GS process technical support team was built on the foundation of expertise developed for the ammonia-hydrogen and amine-hydrogen exchange processes. AECL has maintained this active program in other processes for the entire period that the GS process commanded support for the operating plants. This program lead to the amine-hydrogen process reaching the stage of commercial readiness (2.1, 2.2). It has also lead to the demonstration of a series of hydrogen-water exchange processes based on the CRNL invention of a wetproof catalyst (2.3, 2.4, 2.5, 2.6). Ontario Hydro has also contributed to the monitoring and testing of new ideas (2.7, 2.8). The cross-fertilization of ideas and techniques among the several processes has yielded benefits to all of them. An analysis of the important parameters of the methods considered for heavy water production has been done recently by Rae (2.9).

3. PROBLEMS AND SOLUTIONS

3.1 Process Analysis and Control - A.I. Miller, CRNL

3.1.1 Evolution in the Canadian Heavy Water Industry

The GS process is not a difficult process to understand and can be described fairly accurately by techniques developed for two-component distillation. This approach was used to design the original GS plants in the USA in the 1950's and the details have been described (3.1.1).

The American plants had been built for strategic reasons and had design margins so large that they easily reached around double their rated capacity. Partly in consequence of this overdesign, detail of their actual functioning was obscured. In contrast, the Canadian plants were built for commercial production of heavy water at the lowest possible price. For them, some of this detail was to be important and one critical measurement, the efficiency of the sieve trays, was misinterpreted: this was not as high as construed from measurements at the American plants. In like vein, the process was presumed to be basically non-foamy, although occasional

periods of foaminess had been noted at Savannah River. Design of the Canadian plants with higher gas velocities was to reveal an intrinsically foamy GS system.

In retrospect, these two elements of misinformation stand out clearly but in the early years of frustratingly poor operation of the Canadian plants, they emerged only slowly from a background of many potentially important variations in the Canadian designs. Credit for the understanding belongs to the industry as a whole, including the operators of the American Savannah River plant operated by E.I. DuPont. Fundamental studies of the system's foaminess, work on hydrates, manipulation of plant chemistry and operating conditions, measurement of local densities in the towers using attentuation of gamma rays, and much painstaking analysis of operating data by plant staffs and the industry-wide working parties all contributed to the final mastery. Also contributing to process understanding were very detailed computer simulations of the plants.

Simulation

Steady-state simulation models for heavy water separation processes had first been developed at Chalk River for the amine (aminomethane) - hydrogen process. During 1968 it became apparent that the technique of process simulation might be usefully applied to the GS plants at Port Hawkesbury (in the final stage of construction) and Bruce (under design). In 1969, work began at CRNL to develop a GS simulation. This had its first application in modelling the effects of heat of reaction in the final GS stage and led to some modifications to the Bruce design. In this period, problems with the stability of the model of the exchange tower were gradually overcome so that it was ready, though far from perfected, to be used in the redesign of the Glace Bay Heavy Water Plant for which AECL were given responsibility in 1971. In 1974 the program began to be used to study operating problems for Bruce. Today, in various forms, it is widely used to analyze both real and hypothetical operation for all the operating Canadian plants.

The technique used for the steady-state simulation of the process was based on methods evolved at McMaster University (3.1.2). Figure 3.1.1 is a typical heavy water plant simulation flowsheet and suggests the magnitude of the problem, but the reality also includes process streams of gas and liquid leaving each of the approximately 1 000 sieve trays of the actual plant. The process also is further complicated by very high levels of recycle, deuterium flows up to 60 times the product rate and mass flows thousands of times larger than the product flow. Since most of the typically 2 200 streams are defined only by the conditions of neighbouring streams, a great deal of iteration is required. The operation of each sieve tray is calculated in terms of enthalpy, mass (water and hydrogen sulphide), and deuterium balances and a typical whole-plant simulation would carry out between five and ten million of these calculations before achieving satisfactory convergence. Continuing efforts to improve the performance of the program coding have reduced computer time by about an order of magnitude.

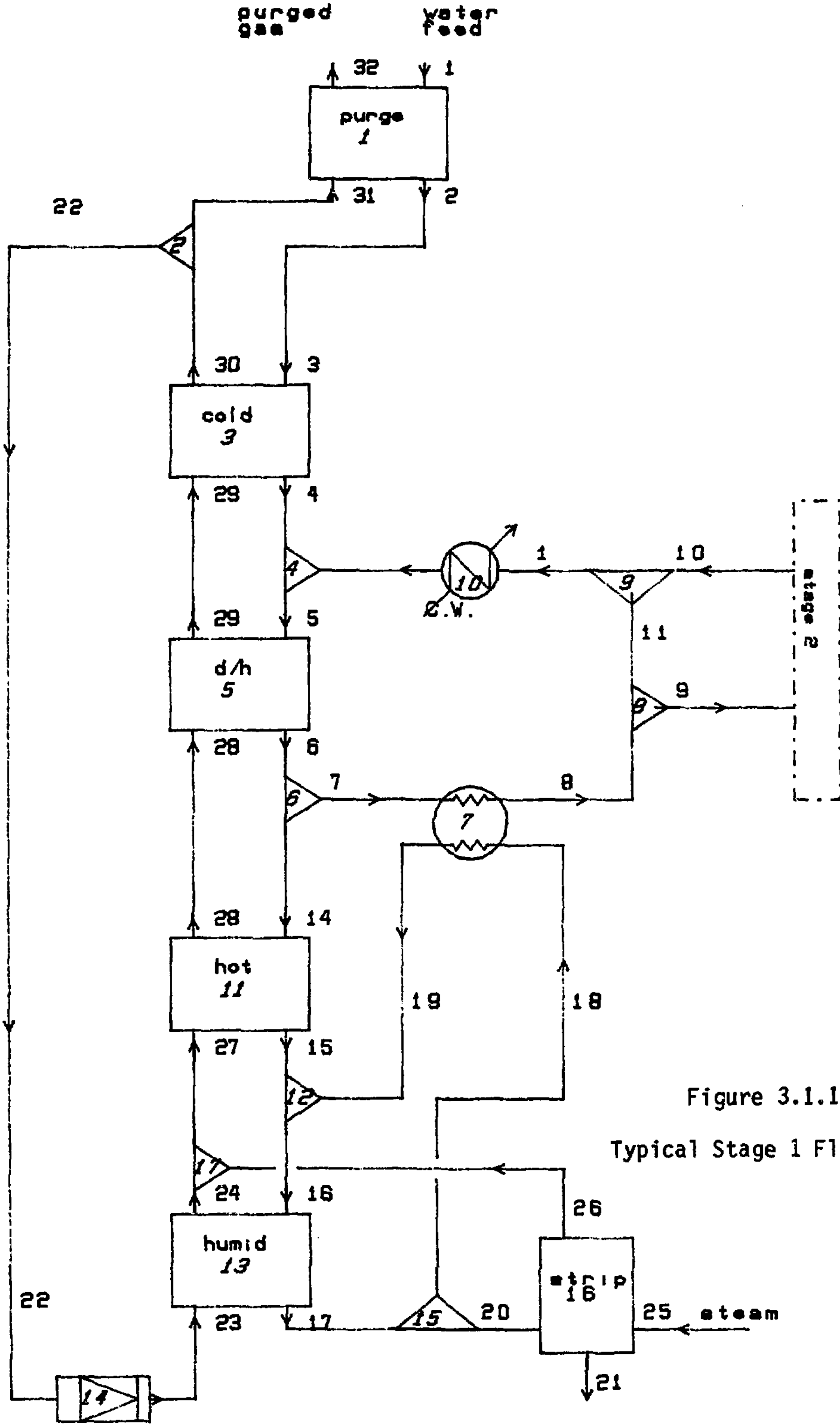


Figure 3.1.1

Typical Stage 1 Flowsheet

The American plants were able to meet their design ratings without recourse to analyses remotely approaching the complexity of the simulation models developed for the Canadian plants. Computer costs during the development and early application of the program were large - several millions of dollars. Commitment of funding on this scale is easy to justify today but at that time needed appreciable foresight to appreciate its ultimate worth.

The reader should realize that the poor performance of the GS plants could be diagnosed by quite simple methods. However, the effect of the plant's tray deficiencies appeared not only as poor extraction but also as much enhanced sensitivity to process parameters. Small perturbations from ideal operation became very important. This was where the detailed simulation first showed its utility: because of its fundamental rigour, the simulation pointed to a number of ways in which plant operation could be improved and what settings should be aimed for and how precisely they should be maintained.

Simulation alone would be academic and sterile. Its utility stems entirely from availability of plant data. The willingness of all of the Canadian plants to vary normal operation to provide data was essential to development of effective models. As important was the instrumentation to monitor plant behaviour. AECL and Ontario Hydro collaborated to retrofit one BHWP tower with extra temperature, deuterium concentration and pressure drop monitoring devices and the redesign of Glace Bay included a similar tower. In addition, operating data for all three plants have been fed into computerized data bases on the CRNL computers. For Port Hawkesbury and Glace Bay data are collected by on-line minicomputers and provide a particularly extensive and invaluable resource for study of normal and abnormal operation. But even with all these resources, simulation would have remained marginally useful if it had not been given life by plant technical and operating staffs. Their knowledge of what actually seemed to happen and what did or did not make sense was and will remain vital to the understanding of analysts using simulation both at plant sites and at CRNL.

Simulation has developed most effectively where several specialists worked together. It is a tool for skilled users and can easily be misinterpreted in inexperienced hands. In particular, isolated individuals have found it difficult to discern when the program was no longer describing a plant realistically.

The GS process R&D program required a comprehensive set of physical properties for the hydrogen sulphide-water system and for pure water at various isotopic concentrations of deuterium. When GS process studies commenced at CRNL in 1969, the properties used initially were those reported by Burgess (3.1.3) but it soon became evident that these were not as accurate as desired, especially with respect to enthalpies. AECL then undertook an extensive review of all available information in 1970-72 and produced a new compilation (3.1.4) which became the recommended standard for the Canadian heavy water industry. This review by AECL drew attention to several areas where information was suspect or not available and as a

result several research contracts were placed with Canadian universities and research organizations to determine new data.

When new information became available the original AECL publication was extensively revised, particularly with respect to solubility and P-V-T data for pure H_2S gas and H_2S-H_2O vapour mixtures. This information was published in 1977 as report AECL-5702 (3.1.5), which remains the definitive source of GS process physical property data.

3.1.2 Applications

3.1.2.1 Plant Operating Performance Analysis

The GS plants operate as one large whole rather than as a sequence of processing stages. Hence it is often difficult to characterize the behaviour of a part of the plant in isolation. Steady-state simulation can give a complete view of the plant by fitting measurements of operation throughout the process into a complete modelling. Then the operation of constituent parts can be assessed and the contribution of their actual or any projected form of operation can be expressed as influences on whole-plant operation.

3.1.2.2 Process Optimization and Control

GS Product Concentration

As one example of performance analysis, the effect of the concentration of the product from the GS process (a complex result of direct and indirect temperature influences) could be described. The simulations justified large reductions in product concentration through measures to augment the finishing capacity of the plants' water distillation finishing units. Extraction gains range from 1 to 2% for Bruce and Port Hawkesbury to exceeding 10% for Glace Bay.

While it seems reasonable to ask whether the effect of product concentration could have been deduced from plant experience, the reality was that such data were extremely misleading through being confused by numerous other variations in plant behaviour that could only be properly unified by the simulation. The actual plant data were, of course, essential to prove and tune the model.

Cold Tower Temperatures

By assuming isothermal behaviour in the major tower sections of a GS plant, simple calculation methods can achieve good approximations to the ideal performance of all but the stage with the highest concentration (i.e. exceeding about 1% heavy water). However, there are small temperature gradients in all stages and the heightened sensitivity caused by low tray efficiency gives these far more importance than expected from the

experience of the American plants. For Glace Bay's cold towers, a temperature rise of one kelvin lowers extraction by 2.4%. But the formation of solid hydrogen sulphide hydrate sets a lower boundary to cold tower temperature and, with this very real boundary, the simulation model can 1) take the sparse array of plant temperatures and produce a complete temperature profile, 2) show the optimum location of the minimum temperature, and 3) provide an essential interpretive tool for probing the lowest attainable value for the minimum temperature.

Plant trials on the heavily instrumented tower at the Bruce plant and their interpretation by simulation led to cold tower temperature reductions of two kelvins (or a 3% gain in extraction) for routine operation for the whole plant. An example of the importance of correct location of the minimum temperature is given in Fig. 3.1.3.

Heat Optimization

The steep temperature profiles (about 100 kelvins over 12 to 15 trays) of the heat transfer sections of the main towers are also amenable to simulation techniques, and usefully so. With the mass transfer trays, measured information on deuterium concentrations is very sparse and only large blocks of trays can be assessed. In contrast, on the heat transfer trays, temperature information is generally more abundant. In the heavily instrumented towers, it is so dense that interpretation of performance data is only limited by apparent variations in temperature across individual trays.

GS plants use large quantities of steam - typically a unit mass of heavy water needs 12 000 times that mass of steam. Rising energy costs have encouraged development of specialized simulations to optimize energy usage. Quite early in the application of simulation, lower than design dehumidifier return temperatures were shown to save 2-4% of steam consumption. Today we are developing a whole-plant heat optimization model for the Port Hawkesbury heavy water plant that will accommodate the performance of individual exchanger banks for each of the three stage-one towers in the complex heat recovery network. One useful development has been presentation of key parameters from the simulation results as graphic output on a computer-drawn flowsheet schematic.

This should remind the reader that simulations are not omniscient black boxes but powerful tools to present the essentials of complex plant operation. Properly used, they indeed provide numerical guidance but they also allow deep insight into plant working.

Other Applications

The same process of plant tests combined with simulation have led to numerous other gains in plant performance by showing how small flow changes and temperature alterations influence extraction. This has been

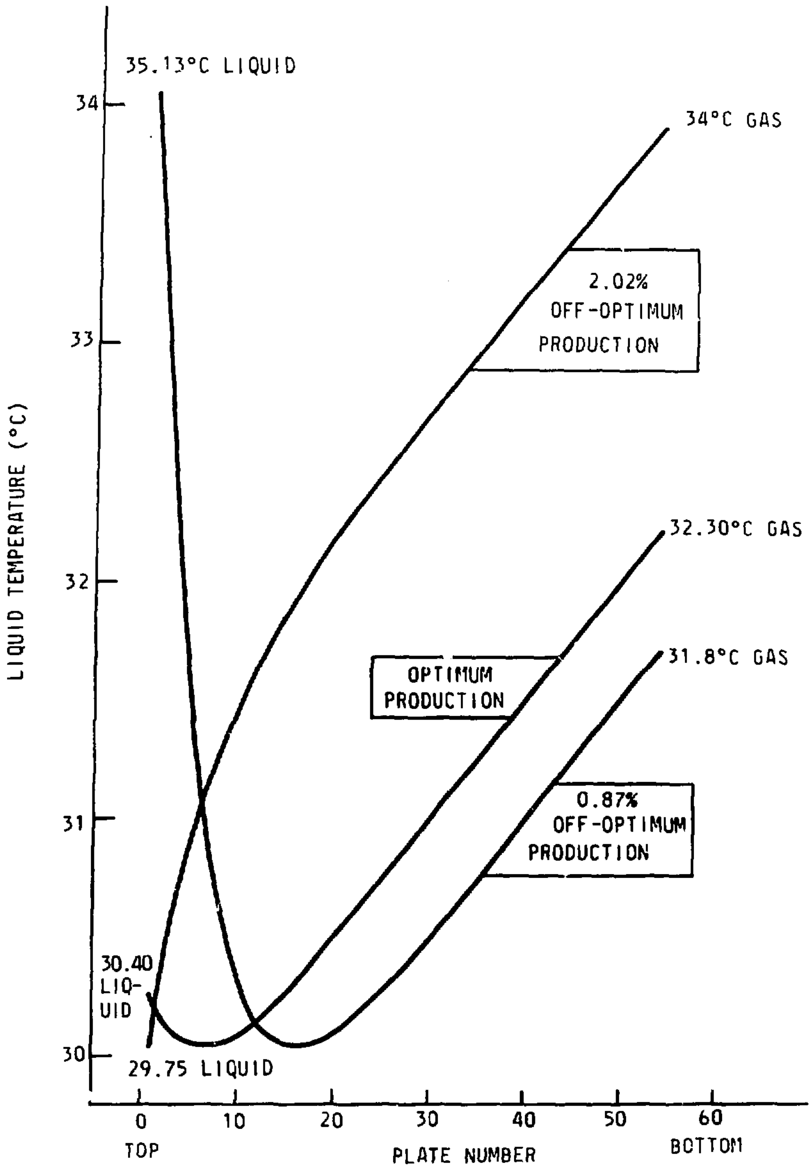


Figure 3.1.3

Typical Cold Tower Temperature Profiles

especially important to Glace Bay, where the presence of very large flows between stages makes process optimization difficult and complex.

The strength of the simulation is always in its ability to describe the plant entirely. From this one can see a) the effect of a local variation on the whole plant and b) local conditions at places in the plant not directly instrumented.

3.1.2.3 Equipment Modification

Very precise descriptions of the actual operation of plants over the full range of operating conditions is useful if one wants to look at possible changes to the plant. As discussed elsewhere in this paper, numerous changes to tray detail have been implemented and recommended. Both trays and plant understanding are needed. The plant simulation first shows the current situation for either deuterium or heat transfer; knowledge of tray design shows how one or other of these might be improved; simulation predicts the effect on operation and finally measures what has been achieved.

This technique has been applied to single malfunctioning trays as well as to whole towers.

3.1.2.4 New Designs

Many fundamental changes to the flowsheets of existing plants have been suggested but the difficulty of implementing these without new tower penetrations has usually been a major factor inhibiting implementation.

However, the understanding of the minutiae of the GS process that the simulations have built up should lead to new plant designs that contain sophisticated improvements and will perform as expected. Partially this sophistication was applied to the design of the suspended LaPrade plant (as in an asymmetric distribution of mass transfer trays between cold and hot towers - calculated to augment production by 0.7%) but the full power of the simulations would also fully exploit the capacity of trays to provide both heat and deuterium transfer exchange. The ability to analyse this is intrinsic to the advanced hot feed designs evolved at Chalk River. Because they depend on deuterium transfer where large variation in temperature exists from tray to tray, evolution of these designs is only possible with detailed simulation. They have the ability to produce 5 to 10% more heavy water per unit of tower volume and per unit of steam.

3.2 <u>Process Chemistry</u> - D.A. Spagnolo, CRNL

The chemistry of the GS process is dominated by the presence of hydrogen sulphide at 2 MPa and the recycle flow arrangement through the two temperature regions of the towers. Under cold tower conditions the system

operates close to the liquefaction pressure of H_2S resulting in inherent foaminess (3.2.1). Foaming can be further enhanced by the presence of certain trace impurities entering with the feedwater. These same impurities, if present at the same concentration, would have a negligible effect if the process were operated significantly further from the H_2S liquefaction conditions.

Impurities can also accumulate to high concentration because of the concentrating action of the process, and this leads to foaming and fouling problems. These impurities may originate in the feedwater or H_2S supply gas or may be the decomposition products of antifoam agents and sealing oils that are used in mechanical rotating seals. They may be too volatile to flow down through the hot tower or the effluent stripper, and not sufficiently volatile to be purged as a gas from the system and so concentrate in the process.

All of the plants have had problems in the area of process chemistry although the severity of specific problems has varied from plant to plant, depending on feedwater characteristics, flowsheet details, materials of construction and chemicals used. An industry-wide Process Chemistry Working Party has met throughout much of the decade as the forum for focusing experience, problems and solutions.

3.2.1 Antifoams

Foaming has been a major problem in the heavy water industry, dating back to the early operation of the USA plants where the need to control foaming with adequate water treatment and with an antifoam agent was first identified. The use of antifoams is essential to maintain plant stability while operating at high throughputs. First sign of instability is usually an increase in column pressure drop which signifies an increase in liquid holdup on the trays caused by downcomer backup of the foam. If not corrected, this leads to instabilities involving severe dumping of the liquid on the trays and loss of heavy water production.

A conventional silicone-based antifoam was initially used in Canada, based on USA plant experience. This antifoam consisted of a water-insoluble silicone oil, surface-active silica particles and organic emulsifiers. The cost was several million dollars per year. Moreover, its use resulted in process problems which appeared only after several years of operation. Emulsifiers, present in the antifoam, hydrolyzed under hot tower conditions to form fatty acids which, because of their volatility, accumulated in the process. When combined with the hydrocarbon sealing oil that leaked into the process the fatty acids formed grease-like semisolids which fouled heat exchangers and caused blocking and foaming problems on the trays.

Two lower cost conventional hydrocarbon-based antifoams were assessed in plant trials at BHWP. The first trial ended when the hydrocarbon oil in the antifoam accumulated in the third stage, causing

severe instabilities. The second trial with a heavier hydrocarbon oil appeared effective during summer operation but was not capable of controlling instabilities during the more foamy winter periods. Both antifoams had the disadvantage of containing emulsifiers capable of breaking down under hot tower conditions to form fatty acids.

An antifoam development program (3.2.2) was started at CRNL in 1977 to find new and more suitable antifoams for the GS process. Early in the program certain nonionic surfactants were identified as effective antifoams under cold tower conditions, even though some of these surfactants behaved as foamers at ambient conditions. Antifoam action was attributed to their limited solubility in aqueous H_2S solutions.

Candidate antifoams are first screened for their chemical stability, volatility and antifoam effectiveness under GS process conditions in the laboratory. Those that pass this initial screening undergo extensive pilot plant testing at various flow, temperature and pressure conditions and over a wide range of antifoam dosage rates. Also, influence on deuterium mass transfer, tray-to-tray entrainment and froth characteristics on the tray and in the downcomer are studied in a 0.3 m diameter sieve tray column in the pilot plant.

Antifoam candidates that pass the extensive laboratory and pilot plant screening are further assessed during sequence of trials of increasing duration at a production plant. During these trials, the influence of the antifoam on froth height, tray efficiency, out-of-column entrainment, plant production and accumulation of antifoam or reaction products are measured and related to plant performance. Four such nonionic surfactants have progressed to the stage of having undergone production plant trials; two are presently in regular plant use. Table 3.2.1 summarizes the status of these antifoams.

The silicone-based nonionic surfactant (Antifoam B) has been in use at BHWP and PHHWP since 1978. Its benefits over the conventional type of antifoam (A) are higher D_2O production because of fewer foam-related process problems, and a factor of four reduction in antifoam consumption resulting in an antifoam material saving of $700 000 per year for both plants combined.

GBHWP did not respond so favourably to the use of Antifoam B, although performance was still better than with the conventional one. Dosage rates were higher and operating stability poorer. Further laboratory and pilot plant work revealed that at the more severe conditions of the effluent stripper at GBHWP, the antifoam decomposed to form products that were foaming agents under GS cold tower conditions.

This led to plant trials at GBHWP in 1980 of two new hydrocarbon nonionic surfactants (Antifoams C and D). The trial with Antifoam D was the most successful. Dosage rates were reduced by a factor of almost two with improved plant stability by eliminating the foam-causing decomposition

Table 3.2.1

Antifoam Usage

Antifoam	Type	Relative Dosage	Relative Usage Cost	Plant Usage
A	conventional silicone based antifoam	1.	1	originally used at plants
B	silicone based non-ionic surfactant	0.25	0.20	presently used at PHHWP & BHWP
C	hydrocarbon based nonionic surfactant	0.25	0.06	has undergone plant trial at GBHWP
D	hydrocarbon based nonionic surfactant	0.5	0.12	presently used at GBHWP
E	hydrocarbon based nonionic surfactant	0.5	0.12	presently undergoing plant trials at BHWP

products of Antifoam B. The antifoam was also four times cheaper than the silicone-based surfactant, resulting in an antifoam material saving at GBHWP of approximately $500 000 per year. Moreover, improvement in stability and overall plant performance resulted in a production gain of approximately 7%. BHWP is presently undergoing a plant trial with another hydrocarbon-based surfactant (Antifoam E) which is generically similar to Antifoam D.

Work continues on developing better and cheaper antifoams for heavy water plants with possibly more emphasis on improving mass transfer performance.

3.2.2 Behaviour of Impurities

Studies of the mechanisms for concentrating or eliminating impurities from the process system were initially undertaken to predict the behaviour of oil in the process. Oil is used in the mechanical seals for rotary pumps and blowers to prevent leakage of hydrogen sulphide gas to the atmosphere. Oil accumulation in the process by in-leakage can lead to plant instability.

A model was developed at CRNL to describe the behaviour of impurities, which is largely determined by the relative volatility with respect to hydrogen sulphide.

$$\alpha = K \text{ impurity}/K\ H_2S$$

where K = vapour - liquid equilibrium constant (y/x).

The model predicts that impurities with K-values close to the L/G ratio in the tower concentrate between hot and cold towers. This buildup leads to instability if the impurities are foamers at the process conditions.

When applied to the fatty acids produced from the breakdown of emulsifiers in the conventional antifoam the model predicts accumulation in the higher stages. It also shows that with the existing flowsheet the only mechanism to remove the fatty acid is via the oil coalescer downstream of the third stage tower, but since the flow through this coalescer is only a small fraction of the total third stage contents it is incapable of removing fatty acids at sufficient rates. Analysis of the oil removed by the coalescer at BHWP and GBHWP gave fatty acid concentrations of approximately 45 g/kg and 130 g/kg, respectively, confirming the behavioural prediction of the model.

3.2.3 Sulphur Formation and Control

Sulphur is an in-process impurity that causes production incapability. It accumulates as a solid mainly in two areas: 1) heat exchangers and piping of the dehumidifier circuit and 2) overhead gas coolers and knock-out drums of the purge and stripper system.

Sulphur is formed mainly by the oxidation of hydrogen sulphide by the oxygen that remains dissolved in the feedwater after the degassing operation.

$$H_2S + \tfrac{1}{2}O_2 \longrightarrow H_2O + S$$

A second source of sulphur can be the decomposition of hydrogen sulphide.

$$H_2S \rightleftharpoons H_2 + S$$

Decomposition is favoured in the effluent stripper where the temperature is highest and the hydrogen concentration is low.

There are a number of solutions to this problem:

1) improved degassing of the feedwater,
2) design of equipment to accommodate sulphur accumulation, and
3) chemical techniques to control the formation rate of sulphur.

The second solution, extensively used at the Savannah River Plant (SRP) in the USA, is currently favoured although it eases rather than solves the problem.

Two promising chemical techniques have been assessed in the laboratory. They are 1) the addition of sodium sulphite with catalyst to the feedwater to scavenge residual oxygen, and 2) the addition of hydrogen to the gas systems to reverse the hydrogen-sulphide decomposition reaction.

3.3 Analytical Chemistry - W.J. Holtslander, CRNL

Analytical chemistry serves an important function in the operation of the heavy water production process. Analysis of the deuterium concentration in process water provides the information necessary for the fundamental control of the process flows. Proper control of these gas and liquid flows govern the deuterium extraction rate. The hydraulic behaviour of the water-H_2S mixture in the process towers is sensitive to trace amounts of impurities so that knowledge of the purity of these streams is important.

The deuterium molar concentration in water must be measured over a wide range from 118 parts per million to 99.8 percent. To cover this range methods based on mass spectrometry, infrared spectroscopy, density and refractometry have been developed. Both methods and instrumentation were extensively investigated to provide reliable systems for plant operations. Industry-wide standards with accurately known deuterium concentrations were prepared at CRNL and used for interlaboratory comparisons between the plants and CRNL. Deuterium concentrations in the hydrogen sulphide gas was also required for measuring sieve tray efficiencies. Methods of doing this difficult analysis for both wet and dry gas were successfully developed. This analysis method has allowed the key work on tray efficiency to proceed.

The toxicity of hydrogen sulphide meant careful monitoring of its presence in air was essential. Work at CRNL was carried out to evaluate commercial monitors for this critical application and to define a reliable system that has been applied in both plants and laboratories.

The major emphasis on process analytical chemistry stemmed from the severe foaming problems encountered in the early operations of the Port Hawkesbury and Bruce plants. It was believed the foaming was caused, at least in part, by impurities being added to the process through either the feedwater, the H_2S make-up, or both.

To co-ordinate this analytical chemistry effort a group of chemists from the three heavy water plants, the Nova Scotia Research Foundation, the Chalk River and the Whiteshell laboratories and the General Electric Research and Development Centre in Schenectady, N.Y., was formed. Subsequently chemists from Ontario Hydro Research and the Savannah River heavy water plant participated occasionally. The group meets twice a year on a continuing basis.

A major sampling and analysis program was set up between Bruce HWP and CRNL to provide information on the impurities in the major process streams throughout the plant. Samples were taken once a week and shipped to CRNL for analysis. This program provided a baseline of impurity levels

and their movement throughout the plant during both stable and unstable operation. The data generated by this program was deposited in a computer-based data system from which it could be retrieved in graphical or tabular form.

This, and similar programs at the Glace Bay and Port Hawkesbury plants, identified many problems in obtaining reliable analytical results from plant samples. One of the major problems was obtaining representative samples of the process streams and preserving these samples until they reached the laboratory for analysis. This was particularly severe for the determination of impurities with a volatility intermediate between that of water and the H_2S. Samples could not be taken in open sampling bottles because an unknown fraction of the volatile impurities would be lost, making the subsequent analytical results meaningless. This problem was solved by sampling into stainless steel cylinders at process pressures. Special precautions were then taken to analyse the entire sample.

The second major problem was that established chemical analysis methods did not always apply to samples containing H_2S, water and various sulphur impurities. For example there are many methods available in the open literature for the determination of trace sulphur containing compounds in air, but there are very few methods published for the determination of trace quantities of these impurities in essentially pure H_2S. As a result, special methods were developed by chemists at the plants and in the research laboratories and assembled in a manual of standard analytical methods for the heavy water industry. Table 3.3.1 lists the contents of this manual.

Since many of the analytical methods had been specifically developed for GS process samples the accuracy and precision were not established. For comparison of data from one plant to another it was necessary to establish the accuracy and precision through formal interlaboratory comparison using standard samples. Standard published ASTM procedures for carrying out interlaboratory comparisons were followed.

Many of the methods for analysing special samples require the use of sophisticated analytical instrumentation (3.3.1, 3.3.2, 3.3.3). Other analyses, required for normal day-to-day operation of the plant, are done in the plant laboratories. Originally all of the special samples were sent to the research laboratories, but because of sample preserving problems most of the plant laboratories were eventually equipped with some special equipment. Typical instrumentation in the plant laboratories includes mass spectrometers (exclusively for deuterium analysis), infrared and atomic absorption spectrometers, gas and liquid chromatographs, as well as conventional laboratory equipment. Some special analyses are still done in the research laboratories.

Some examples of the applications of analytical chemistry to process problems follow. One early problem was the deposition of a scale

Table 3.3.1

Standard Chemical Analysis Methods for the GS Process

Acidity (water)
Alkalinity of water and waste water
Aluminum (water)
Aluminum sulfate
Ammonia (water)
Atomic absorption-atomic emission spectrometry for metals - Al,Ca,Cr,Cu,Fe,Mg,Mn,Si,Na
Calcium (water)
Carbon dioxide (water, gas)
Carbonate (water)
Chemical oxygen demand (water)
Chloride (water)
Coagulant aid
Colour (water)
Conductivity (water)
Dew point
Deuterium oxide (water)
Foam test
GS process gas impurities (H_2S)
Gas sampling cylinders
Hydrazine (water)
Hydrogen sulphide (water)
Methanol (water)
Moisture (solids, gases)
Nitrate (water)
Oil (water)
Organics (water)
Oxygen (water)
pH (water)
Phenolic compounds (water)
Phosphorous (water)
Silicon (water)
Siloxanes (water)
Specific gravity
Sulphate (water)
Sulphide (water)
Sulphite (water)
Sulphur (water)
Total organic carbon (water)
Turbidity (water)
Total solids (water)
UV254 absorbance (water)
Water (oil)

on surfaces such as tower trays and heat exchanger tubes. A detailed analysis of sample deposits from more than 60 plant locations were characterized in terms of composition, structure and morphology. This work was done at the Whiteshell Nuclear Research Establishment (WNRE) using highly specialized applications of electron microscopy, emission spectrography, x-ray diffraction, thermogravimetry and combustion analysis. This study showed iron sulphides were the major constituents of the deposits where H_2S and water were present and iron oxides where H_2S was not present with the water. Pyrite was the most prevalent iron sulphide. Elemental sulphur was also found (3.3.4, 3.3.5, 3.3.6).

Detailed analysis of the feedwater was done to identify impurities that may have contributed to foaming and unstable operation. The impurity levels were very low, particularly for organic compounds, so that a preconcentration step was required to bring the impurity concentrations up to detectable levels. These very low concentrations in the feedwater were important because of the unique ability of the heavy water process to concentrate some impurities within the plant. The preconcentration was done by passing a large volume of water through a carbon bed. The impurities were then extracted from the carbon with different solvents and the solvents analysed. This program was co-ordinated, and the analysis done by the Nova Scotia Research Foundation. This resulted in a compilation that contained 172 different compounds classified by organic groups. Some of these species were shown to contribute to the water foaminess but the removal of no single compound or group of compounds would have eliminated the foaming problem. The practical solution was the addition of antifoams to the feedwater (see Section 3.2). Methods were developed for analysis of antifoam in the process to monitor its decomposition and movement throughout the plant. Some antifoam agents decomposed in the process and required the development of new methods of analysis for both the antifoam and the decomposition products.

Special analyses are required for pilot plant operation at CRNL. One is a method to measure the deuterium concentration in H_2S to determine sieve tray efficiencies.

In addition a number of on-line analysers have been developed. These include analysers for monitoring plant effluent streams for trace concentrations (ppb) of H_2S in water (see Fig. 3.3.1), oil in the feedwater to the finishing unit and deuterium concentration in the plant product from the finishing unit. The H_2S-in-water analyser development is an example of the solution to a plant problem conceived by plant people and developed by a contractor to the heavy water industry (3.3.7). A second commercial H_2S-in-water analyser was modified and further developed in a co-operative program between CRNL and GBHWP (3.3.8). Both types of analysers have been found to be suitable to several applications at heavy water plants.

Further application of on-line analysers is continuing. A deuterium-in-water analyser originally developed as a heavy water leak

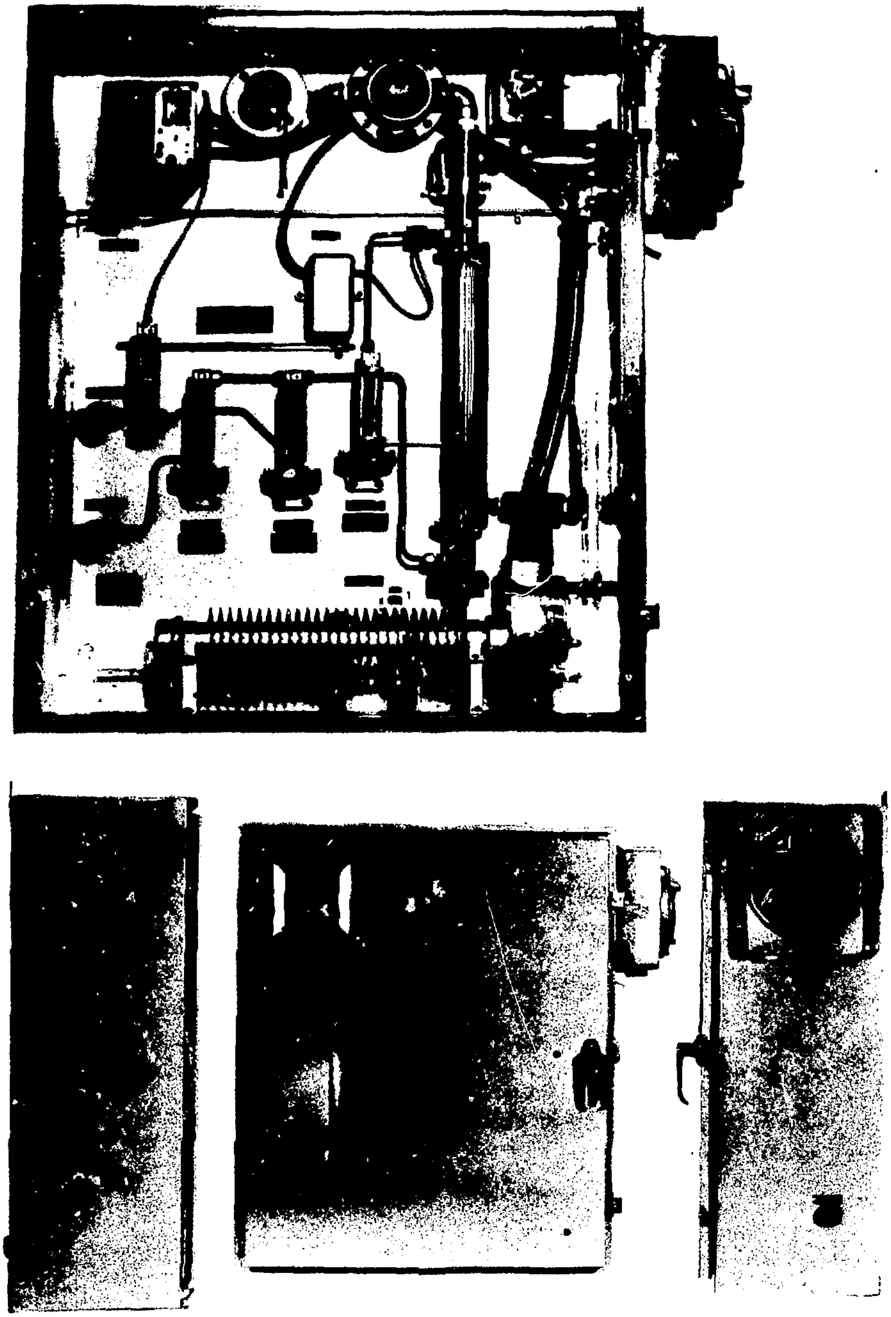


Figure 3.3.1: On-Line H_2S-in-Water Effluent Analyser Manufactured by Nova Scotia Research Foundation Corporation

detector in CANDU (CANadian Deuterium Uranium) reactor systems is being adapted to monitor the difference in concentrations of the feed and effluent streams at GBHWP. This will provide an on-line indicator of plant extraction.

3.4 Materials, Corrosion and Iron Transport - G.F. Taylor, and R.S. Pathania, CRNL

3.4.1 Introduction and History

The selection of materials for the Canadian heavy water plants (3.4.1, 3.4.2) was, at first, based on experience at the US plants and the research and development carried out in their support (3.4.3). Initially materials research in Canada focused on extending the application of some materials, e.g. raising the velocity limit on carbon steel and testing elastomers that had not been previously available. As more plants were built and more laboratories became involved in materials research a GS Materials Working Party was created to aid information flow. In particular, it was necessary to get 1) the experience of each operating plant into the others, 2) the experience of the operating plants into the design and operation of the new ones and into the laboratory programs and 3) the information from the laboratory programs back into the plants.

To this end the materials engineers from the plants, the design companies and the laboratories have met two or three times a year since 1971. By rotating the meeting place among the plant and laboratory sites the working party members were able to examine for themselves the facilities and work in progress at each place. During the ten years of operation of the GS Materials Working Party a few problems have arisen which required a more intensive and co-ordinated effort from plants and laboratories. In each case a smaller task force was formed and charged with finding solutions to an individual problem. Examples are the Iron Transport Task Force and the Impeller Task Force.

The information generated by ten years of effort by the materials engineers and scientists currently resides in numerous journal publications, conference proceedings, internal laboratory reports, plant inspection reports and minutes of meetings. An attempt has been made to consolidate the plant experience in an industry-wide summary and the laboratory personnel are committed to a similar summary of their work. Together these documents will form the base of materials selection decisions for both new and operating plants. In the rest of this section a short summary is provided.

3.4.2 Applications

3.4.2.1 Carbon Steel

In a GS heavy water plant the major use of carbon steel is for towers, piping and heat exchanger shells, though the shells are frequently

clad or lined with stainless steel. Typically ASTM A516 and A333 are specified for plate and pipes, respectively.

The simple concept of carbon steel quickly forming a protective and chemically stable film of iron sulphide and thereafter corroding at a very low rate was supported by the early operation of Port Hawkesbury HWP and laboratory testing. The laboratory measurements suggested that the film could withstand higher liquid flowrates than the seven feet per second to which the plants had been designed. A few failures occurred in the plants downstream of control valves and other locations of high turbulence, indicating that there is indeed a limit to the mechanical stability of the film, and new designs continued to acknowledge the seven feet per second limit as a generally useful criterion. In 1973 carbon steel piping in liquid service at Bruce HWP was found to be corroding rapidly at locations which were not considered particularly turbulent. In addition considerable deposition of iron sulphide was found on stainless steel trays and heat exchanger tubes. The iron had been released from corroding carbon steel. Neither the corrosion nor the deposition diminished significantly with time, contrary to the accepted theory and contrary to the observation at Port Hawkesbury. Shutdowns for cleaning and line replacement reduced the production of heavy water. A large intersite program, involving staff at the laboratories and the plant, was begun to increase our understanding of the corrosion and deposition processes. Three years of effort involving at its peak twelve scientists and engineers resulted in a good understanding of the processes (3.4.4, 3.4.5, 3.4.6) and a technique to minimize iron transport (3.4.7). It was found that the initial corrosion product on steel, mackinawite (FeS_{1-x}), is not protective but transforms to troilite and then pyrrhotite and pyrite. Only the latter two are protective. Process conditions including dissolved iron concentration, liquid velocity, pH and temperature were found to influence the rate of transformation. A pre-conditioning treatment to passivate the carbon steel surfaces of a heavy water plant was developed in the laboratory, tested in the plant and applied successfully to two new units of Bruce HWP.

Hydrogen Blistering

Atomic hydrogen formed by the corrosion reaction can diffuse through the steel. If the hydrogen atoms encounter significant voids or inclusions the rate of diffusion through the steel is slowed allowing hydrogen atoms to join and form molecular hydrogen gas pockets. The pressure of hydrogen is sometimes sufficient to deform the steel forming blisters. As blisters grow ductile tearing and step-wise cracking can ultimately damage the integrity of the vessel.

Hydrogen blistering has been controlled by chemical specification of the steel as well as ultrasonic testing of plate. At BHWP this was quite successful for Plant A. Very little hydrogen blistering was found in the enriching units. Areas of high corrosion such as absorber tower trim sections and rundown tanks suffered some hydrogen blistering which led to the replacement of these vessel sections. In other locations hydrogen damage was controlled by drilling into the isolated blisters to relieve the

gas pressure. In 1977 work started at Ontario Hydro Research to improve the selection or protection of carbon steel to resist hydrogen damage.

BHWP B was built with steel to the same specification as BHWP A but hydrogen damage has been much more extensive. The absorber and purge towers in both E3 and E4 were replaced in 1980 due to hydrogen blistering following fairly short exposure to H_2S. (E3 four months, E4 one year). Hydrogen damage has been found in other towers and vessels so further replacement or repair may be required.

Because of the research program ongoing from 1977, new tighter specifications, tests and inspection techniques are available for the selection of replacement steels. These purchase specifications were used for the replacement steel for the absorber and purge tower in BHWP B. The revised specification would be applicable to any new heavy water plant construction.

3.4.2.2 Stainless Steel and Nickel Alloys

In a GS plant stainless steels are used for piping, heat exchanger tubes and liners, impellers, valve stems, etc. Nickel-base alloys are used in applications such as bellows, springs and diaphragms. Although the experience with stainless steel and nickel alloys in H_2S service has generally been satisfactory, occasional failures have occurred due to localized corrosion, e.g. stress corrosion cracking (SCC) and pitting corrosion. The factors responsible for localized corrosion of stainless steel and nickel alloys in H_2S-saturated water have been identified through research programs and failure investigations in various laboratories.

Stress Corrosion Cracking

Both intergranular and transgranular stress corrosion cracking of stainless steels have been observed in H_2S-saturated water. Intergranular SCC may occur in sensitized stainless steels and nickel alloys when they are exposed to sulphur-oxy acids (e.g. polythionic acids, sulphurous acid) formed by interaction of sulphides, moisture and oxygen. Stainless steels may be sensitized (a condition characterized by precipitation of chromium carbide along the grain boundaries and depletion of chromium adjacent to the grain boundaries) during welding or heat treatment. A study showed that stressed types 304 and 316 stainless steels, heated at 650-760°C for one hour and exposed to a solution containing H_2S and air failed by intergranular SCC. However, types 304L, 316L and 321 stainless steels were resistant to SCC under the same conditions. Similar behaviour was observed in a solution containing polythionic acids. Types 304L and 316L stainless steels are resistant to sensitization because of their low (<0.03 wt%) carbon contents. Type 321 (and type 347) contain carbide stabilizers which minimize the formation of intergranular chromium carbides. Nickel alloys such as Inconel-625 are also resistant to sensitization.

The startup of BHWP B was delayed for two years due to a series of materials failures. The major problem was failure of the expansion joints in the large diameter blower suction lines which suffered from stress corrosion cracking. The initial failure in October '78 and the subsequent failure in Febuary '79 of a rebuilt joint were both due to cracking at the transition zone where Inconel bellows were welded to carbon steel piping. These expansion joints were replaced by all-Inconel joints which also suffered from cracking. The major cause in this case was sensitization of the alloy due to improper heat treatment. To avoid further problems all the expansion joints in BHWP B have been replaced with expansion loops in the large diameter carbon steel lines.

The following steps can help to control intergranular SCC in H_2S environments.

a) For welded applications low carbon or stabilized stainless steels should be used. The welds should be solution-annealed or stress-relieved to minimize residual stresses.

b) The residual H_2S in stainless steel equipment should be neutralized before exposure to air.

Transgranular stress corrosion cracking has been observed in the presence of H_2S, chlorides and air at ambient temperatures and pressures. For example, stressed types 304 and 316 stainless steels exposed to H_2S-saturated water containing 500 mg Cl^-/kg H_2O and oxygen suffered transgranular SCC in 1 600 and 6 000 h, respectively. However, no cracking was observed in a solution containing 500 mg Cl^-/kg H_2O and oxygen but no H_2S. Nickel alloys such as Inconel-625 and Hastelloy C-276 were immune to this type of cracking. Tests also showed that cold-worked type 316 stainless steel was highly susceptible to transgranular SCC.

To avoid transgranular SCC in H_2S environments it is necessary to use annealed austenitic stainless steels and to avoid ingress of air.

Pitting corrosion of stainless steels is most severe in environments containing H_2S, chlorides and oxygen. In the absence of oxygen the rate of pitting corrosion is fairly low. Molybdenum-bearing stainless steels (e.g. type 316) have better resistance to pitting corrosion than type 304 stainless steel. Inconel-625 and Hastelloy C-276 have excellent resistance to pitting corrosion in H_2S environments. These alloys are used in critical applications, e.g. diaphragms and bellows.

3.5 Mechanical Equipment - D.G. Dalrymple, CRNL

3.5.1 Introduction

Equipment design and maintenance philosophies in the nuclear and chemical process industries are similar in some respects, but generally quite different. The major difference is that the design life of major

nuclear power plant equipment such as heat exchangers is thirty years; that of chemical process plant equipment is shorter, typically ten years. This results from the relative ease of replacing chemical process plant equipment. Much of the advanced design and maintenance technology developed in support of nuclear power plants results from applied research and development undertaken because of regulatory requirements, plant maintenance environments, materials of construction, and economic considerations unique to the nuclear industry (3.5.1, 3.5.2). What often results are advances in technology that have wider applicability, since incentives such as increased reliability and reduced downtime also apply in other process industry plants. The purpose of this section is to present a few examples illustrating how nuclear equipment technology has been used in the design and maintenance of heavy water production plants.

In many respects the mechanical equipment problems encountered by the Canadian heavy water production industry are quite compatible with the technology developed by AECL in support of the CANDU nuclear power reactor. This has led to extensive interaction between the two groups in many areas and over many years. The high degree of technical compatibility has generally yielded high return for the R&D effort expended. There has been continuing contact between plant and laboratory staff on mechanical equipment topics that has led to the formation of the industry-wide task forces, covering the topics of valves, inspection and reliability. There is also important liaison on materials of construction through the GS Materials Working Party (see Section 3.4). The goal of R&D activities on these topics is to improve equipment performance, reliability and maintainability.

3.5.2 Applications

3.5.2.1 Heat Exchanger Vibration

The main causes of heat exchanger tube failure are vibration and/or corrosion. Excessive flow-induced vibration may cause tube failure by fretting wear or fatigue. Some degree of flow-induced vibration is inevitable in shell and tube heat exchangers; however, rational design procedures to assure adequate reliability throughout the design life have only recently been developed (3.5.3). These are not generally available, and specifications such as the Tubular Exchanger Manufacturers Association provide little assurance of design life.

There are three relevant flow-induced vibration excitation mechanisms: 1) fluid-elastic instability, 2) periodic wake shedding, and 3) random excitation due to flow turbulence. The objectives of rational vibration design are: 1) avoid fluid-elastic instability, 2) limit tube response due to wake shedding resonance to 2% (rms) of tube diameter, and 3) ensure that fretting wear rates at tube supports, due to impact resulting from tube vibration, are consistent with design life specified.

Such design procedures were not available for initial design of heat exchangers in Canadian heavy water plants. Involvement of CRNL in evaluating and resolving problems encountered in operating plants contributed significantly to development of design procedures. Figure 3.5.1 illustrates five examples in which vibration analysis led to an understanding of problems encountered in process heat exchangers (3.5.4).

To avoid such problems in the future, AECL's heat exchanger vibration design technology has been transferred to Canadian manufacturers of such equipment. In addition, all new heat exchange equipment is subjected to an independent vibration analysis audit at the design stage.

3.5.2.2 Tower and Stack Vibration

A GS process heavy water plant is characterized by high structures such as flare stacks and sieve tray towers which are subject to wind-induced vibration. While vibration response of such structures is incorporated in design, the validity of such analyses depends on the knowledge of such parameters as structural damping, wind-induced dynamic forces, flexural rigidity, and inter-structure coupling. Full-scale vibration experiments by AECL at Glace Bay HWP were undertaken to confirm the design data, and a dynamic model of the inter-connected tower structures was developed. This technology is now incorporated in the design of Canadian heavy water plant structures and provides a degree of confidence in the design consistent with the environmental hazard of hydrogen sulphide.

3.5.2.3 Heat Exchanger Tubesheet Packings

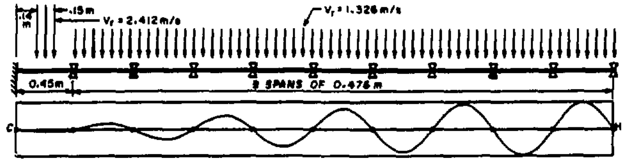
Most heat exchangers in Canadian heavy water plants have floating tubesheets. Considerable difficulty was initially encountered with packing dissolution leading to excessive maintenance. Prior AECL experience with valve packings contributed to one proprietary grade of woven teflon packing being accepted as the industry standard for several years. Subsequent price increases led to a series of six-week laboratory tests on eight similar products to qualify other proprietary grades as generic equivalents. Hard packings generally performed better than soft packings, and packings without spring-loaded gland followers were found to leak profusely after the first thermal cycle (when cold). These tests led to a considerably increased understanding of floating tubesheet packings. In addition, three proprietary grades were identified as being equal in performance, and superior to the other materials tested. Somewhat surprisingly, the three materials recommended on the basis of these tests were superior to the previously preferred material and were about one-third the price.

3.5.2.4 Pump and Compressor Shaft Seals

High priority had to be given to the design and construction of shaft seals used in liquid and gaseous hydrogen sulphide systems. Little directly relevant information as to the performance and reliability of pump and compressor seal assemblies was available at the outset of the Canadian heavy water industry. A number of seal assemblies were therefore tested under simulated service conditions at CRNL (3.5.5). These tests generally

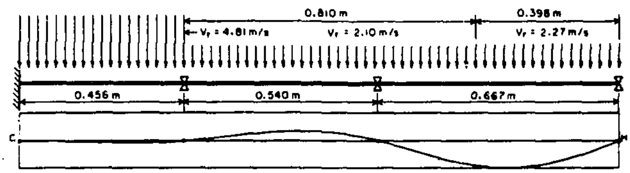
Case DPBC-1: PROBLEM: Outer tube fretting at baffles; SOLUTION: Plug tubes for now and redesign system; FLUIDELASTIC INSTABILITY: No; V_r/V_{rc}=0.77<1; 1st mode, 103 Hz.

d = 12.7 mm
p/d = 1.5
m/ℓ = 0.61 kg/m
EI = 133 N·m²
ρ = 971 kg/m³
c = 5.07 kg·s⁻¹·m⁻¹



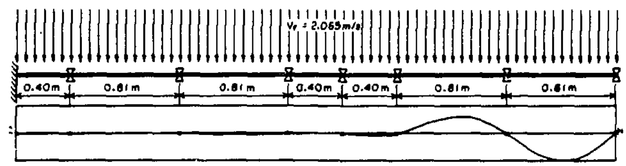
Case PASC-2: PROBLEM: Excessive vibration at 100% flow; SOLUTION: Operate below 60% flow; FLUIDELASTIC INSTABILITY: Yes; V_r/V_{rc}=1.74>1; 3rd mode, 209 Hz.

d = 12.6 mm
p/d = 1.26
m/ℓ = 0.61 kg/m
EI = 130 N·m²
ρ = 998 kg/m³
c = 5.04 kg·s⁻¹·m⁻¹



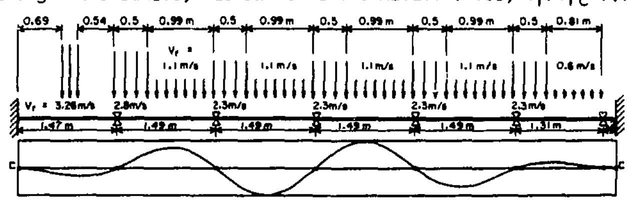
Case PAMX-1: PROBLEM: Tube fatigue & fretting near outlet; SOLUTION: Install lacing rod supports; FLUIDELASTIC INSTABILITY: Yes; V_r/V_{rc}=2.04>1; 1st mode, 37.1 Hz.

d = 12.7 mm
p/d = 1.5
m/ℓ = 0.67 kg/m
EI = 127 N·m²
ρ = 997 kg/m³
c = 5.07 kg·s⁻¹·m⁻¹



Case GBCX-1: PROBLEM: Tube fatigue at tubesheet near inlet, fretting; SOLUTION: Modify inlet now, redesign tube bundle; FLUIDELASTIC INSTABILITY: Yes; V_r/V_{rc}=1.71; 1st mode, 18.2 Hz.

d = 19.1 mm
p/d = 1.25
m/ℓ = 1.20 kg/m
EI = 665 N·m²
ρ = 996 kg/m³
c = 7.63 kg·s⁻¹·m⁻¹



Case PHRC-1: PROBLEM: Tube fretting at supports; SOLUTION: Add supports, modify inlet; FLUIDELASTIC INSTABILITY: at inlet; V_r/V_{rc}=1.37>1; 15th mode, 177 Hz.

d = 19.1 mm
p/d = 1.33
m/ℓ = 1.25 kg/m
EI = 716 N·m²
ρ = 993 kg/m³
c = 7.63 kg·s⁻¹·m⁻¹

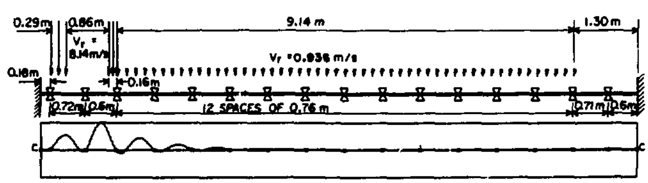


Figure 3.5.1

Five Analyses of Liquid-Liquid Cross-Flow Heat Exchanger Failures

Note of Explanation: V_r/V_{rc} = actual/critical reference gap velocity ratio for the most significant vibration mode in each case ($V_r/V_{rc} \geq 1.0$ indicates fluidelastic instability). The corresponding frequency is specified and the normalized vibration amplitude distribution plotted below for each case. Parameters d, p, M/L, EI represent tube diameter, pitch, mass per unit length and flexural rigidity; ρ, c represent shell-side fluid mass density and viscous damping coefficient. As implied by the data illustrated the first mode is usually, but not always the significant one for heat exchanger vibration design.

indicated acceptable rates of seal face wear could only be achieved at low balance ratio, and that leakage rates would remain acceptably low under these conditions. This early learning experience (based on many years of pump seal research and development dedicated to achieving a five-year life for the seals of the main coolant pumps in CANDU reactors) has contributed significantly to plant productivity, and relatively few pump and compressor shaft seal problems have been encountered.

3.6 Sieve Tray Hydraulics and Mass Transfer - K.T. Chuang, H.J. Neuburg, and D.A. Spagnolo, CRNL

3.6.1 Industry Needs

Sieve tray design for Canadian heavy water plants was originally based on technology derived from systems other than GS, and on the operating experience of existing US heavy water plants. GS plants in the USA at Dana and Savannah River have towers up to 3.5 m in diameter, and Canadian plant design had to be scaled up for sieve trays up to 8.5 m in diameter. In the early stages of operation, Canadian heavy water plants were plagued by cold tower tray instability. It was also soon apparent that mass transfer tray efficiency was lower than the design values, which were based on measurements performed at the Dana plant (3.6.1). As a result throughput and extraction were far below design levels.

An R&D program was required to improve sieve tray performance at the heavy water plants. The objective was to develop reliable correlations which could be used to design and predict the performance of GS process sieve trays. This program represented a large cooperative effort between personnel from CRNL, Ontario Hydro, Nova Scotia Research Foundation, heavy water plants, tray vendors and Canadian universities. Due to the open exchange among these groups, unnecessary duplication of effort was avoided and an extensive range of studies from the behaviour of single bubbles to tests with plant scale trays was possible. Periodic meetings of the Tray Mass Transfer Working Party, where most of these groups actively participate, are held to discuss the R&D results and tray-related problems and activities at the plants. Future programs that satisfy the needs of the heavy water industry are also defined.

3.6.2 Test Program

Tray hydraulic parameters have been investigated in air/water test rigs up to 6.1 m in diameter, and also in a pilot plant at CRNL containing 0.3 m diameter trays operating at GS process conditions (see Fig. 3.6.1). At BHWP and GBHWP first stage towers have been selected to study tray behaviour, and have been fitted with extra instrumentation. Tray efficiency measurements were made at the pilot plant for a wide range of operating conditions and tray variables. A single-hole bubble column and a wetted wall column were also used to learn about the fundamentals of the GS exchange process.

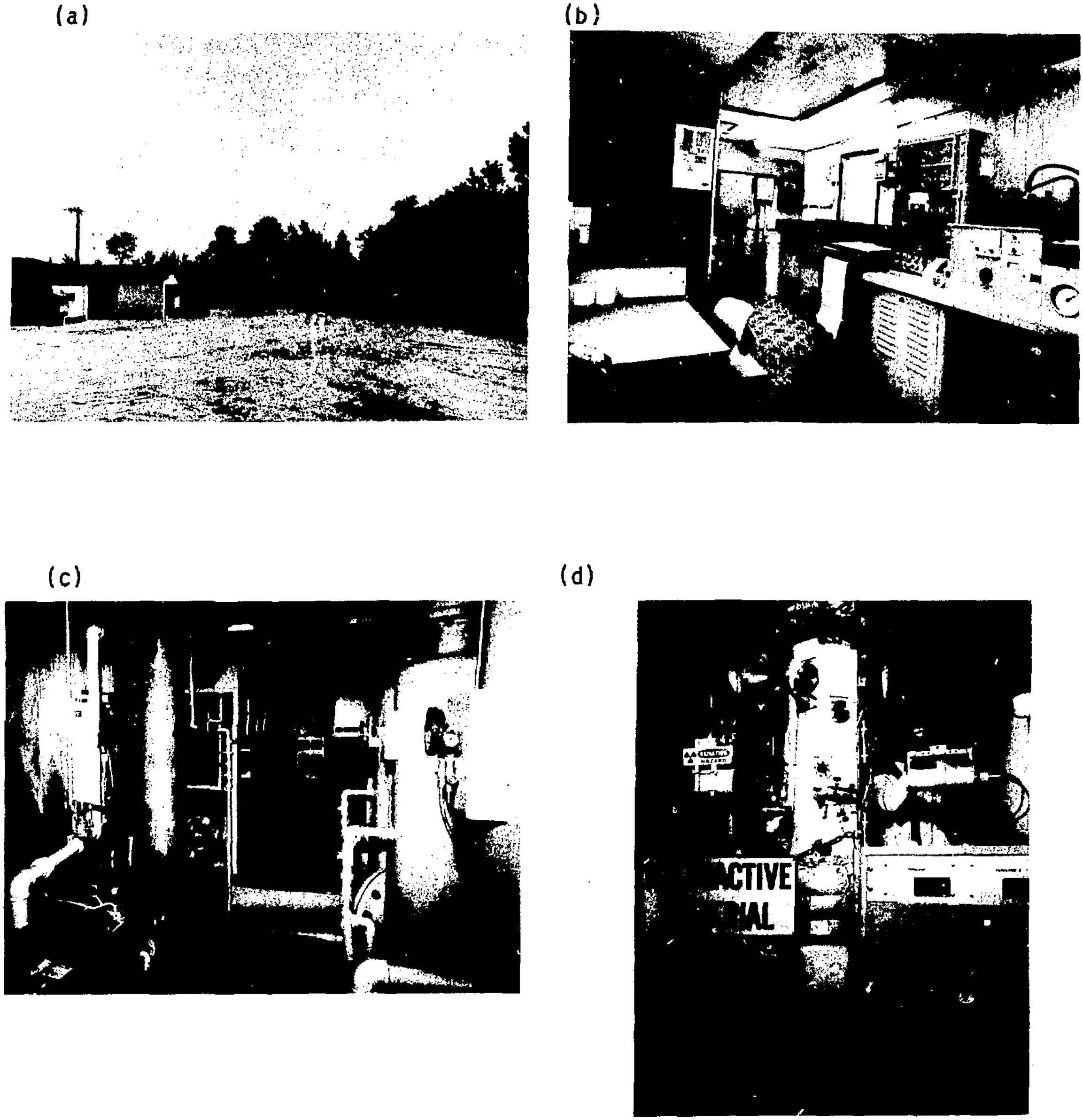


Figure 3.6.1 GS Mobile Pilot Plant at CRNL showing
a) general view of site with workshops and trailers
b) mass spectrometer deuterium analyser
c) water treatment equipment, and
d) GS process equipment with gamma scanning facility mounted on test column.

Most of the tray-related problems encountered at the plants have been identified and solved, and a program has been established to gradually upgrade tray performance according to the needs defined by economics. Laboratory, pilot plant and production plant experience has been used to define and confirm correlations for 31 tray design parameters. This assembled information is used for tray modifications. The R&D effort is expected to continue at the present level for the next five years, with emphasis on new development, such as heat transfer tray efficiency.

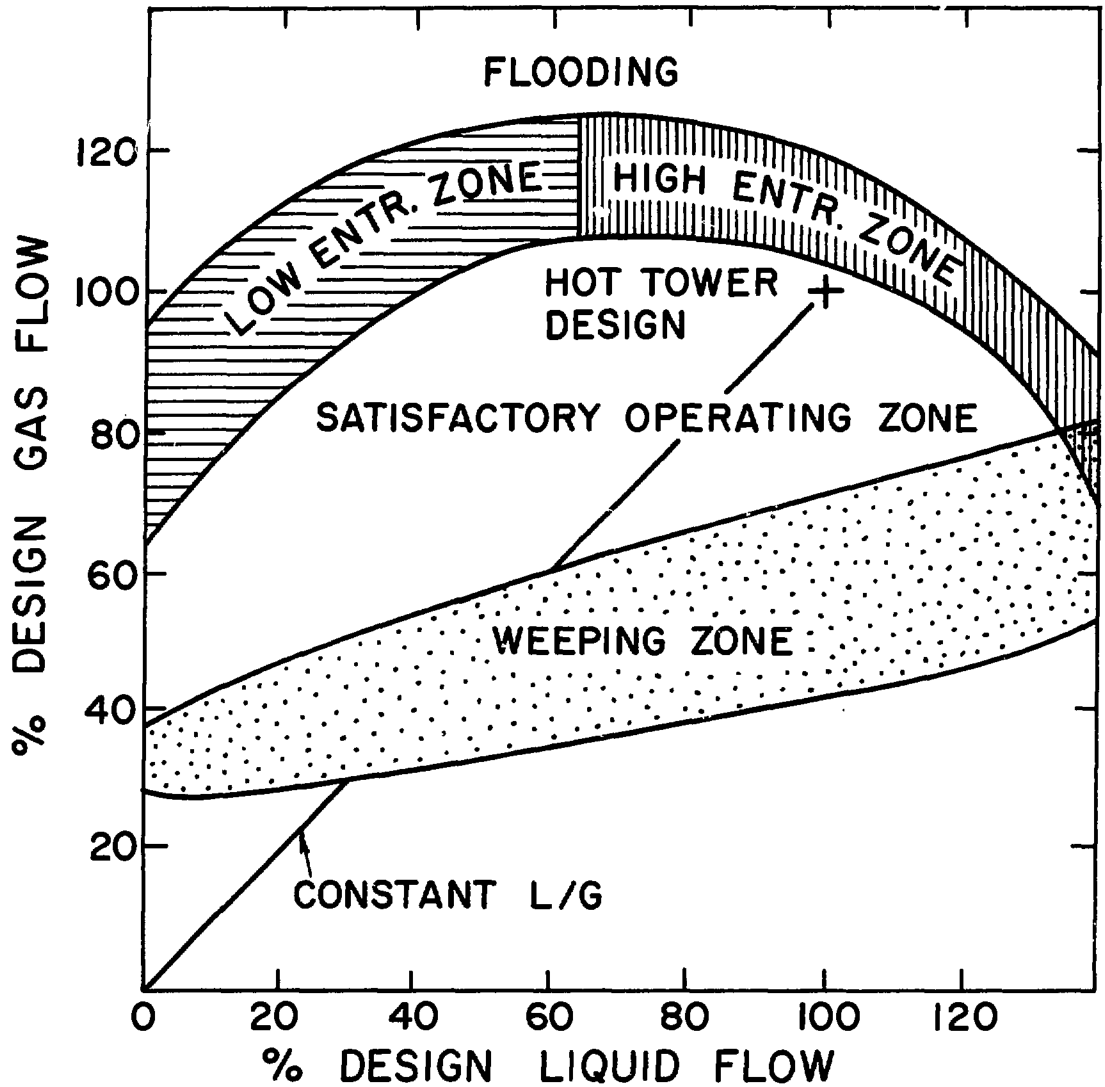
3.6.3 Tray Hydraulics

The two important considerations in tray design are stable hydraulic operation and maximum extraction at design flow conditions. Figure 3.6.2 is a performance chart for a typical hot tower sieve tray, where the satisfactory operating zone is confined within limited ranges of gas and liquid flow rates. Furthermore, GS process operation is restricted to a fixed L/G line as indicated. Deviation in L/G must be maintained within 0.5% to achieve maximum extraction. The ultimate capacity of sieve trays is determined by high entrainment because it reduces the apparent tray efficiency by recycling liquid to the tray above. In GS towers, a loss of 5% production can occur with 3.5% entrainment (defined as kg liquid entrained/100 kg gas) due to reduced hot tower tray efficiency. At turndown conditions, excessive flow of liquid through the perforations (weeping) represents a lower operating limit. Weeping is detrimental to tray efficiency because it reduces gas-liquid contact. When inlet weeping predominates, liquid by-passes two trays causing efficiency to drop sharply. Based on data collected at GS conditions, reliable correlations have been derived to predict entrainment and weeping for industrial trays operating in wide flow ranges.

Tray hardware design combined with effective antifoam agents are the key factors for optimum sieve tray performance. Outlet weir height plays an important role in controlling froth height which also depends on liquid weir loading and gas flow. The higher the froth height the higher is the tray efficiency, up to the point where heavy entrainment occurs. High froth heights also cause higher tray pressure drops, which in turn can result in downcomer back-up problems for foamy systems. Trays originally installed in the Port Hawkesbury and Bruce cold towers were modified during early operation to prevent flooding by reducing the height of the outlet weirs. These changes increased the flow limit from below 90 to above 120% of design flow. It is believed that some of these changes went too far in sacrificing efficiency for stability so that gains in efficiency are possible by increasing weir height. In early days froth heights on GS sieve trays were predicted using a correlation obtained from air/water data measured on a large scale simulator (3.6.2). More recently, a new correlation was derived to predict froth height on GS trays by making use of a large data bank from gamma scanning at the heavy water plants. The same data were used in conjunction with plant pressure drop measurements to derive a tray pressure drop correlation.

Trays have to be designed to contain sufficient downcomer area to prevent choking by the froth flowing into it. Liquid residence time in the

FIGURE 3.6.2 - TYPICAL SIEVE TRAY PERFORMANCE CHART



downcomer must be large enough to allow complete gas/liquid separation between trays. This may be a problem for a foamy system. Downcomer residence time can be optimized by proper setting of the downcomer clearance (underflow weir). However, caution must be exerted to prevent downcomer back-up. Suitable expressions have been derived to calculate the various parameters that affect downcomer performance.

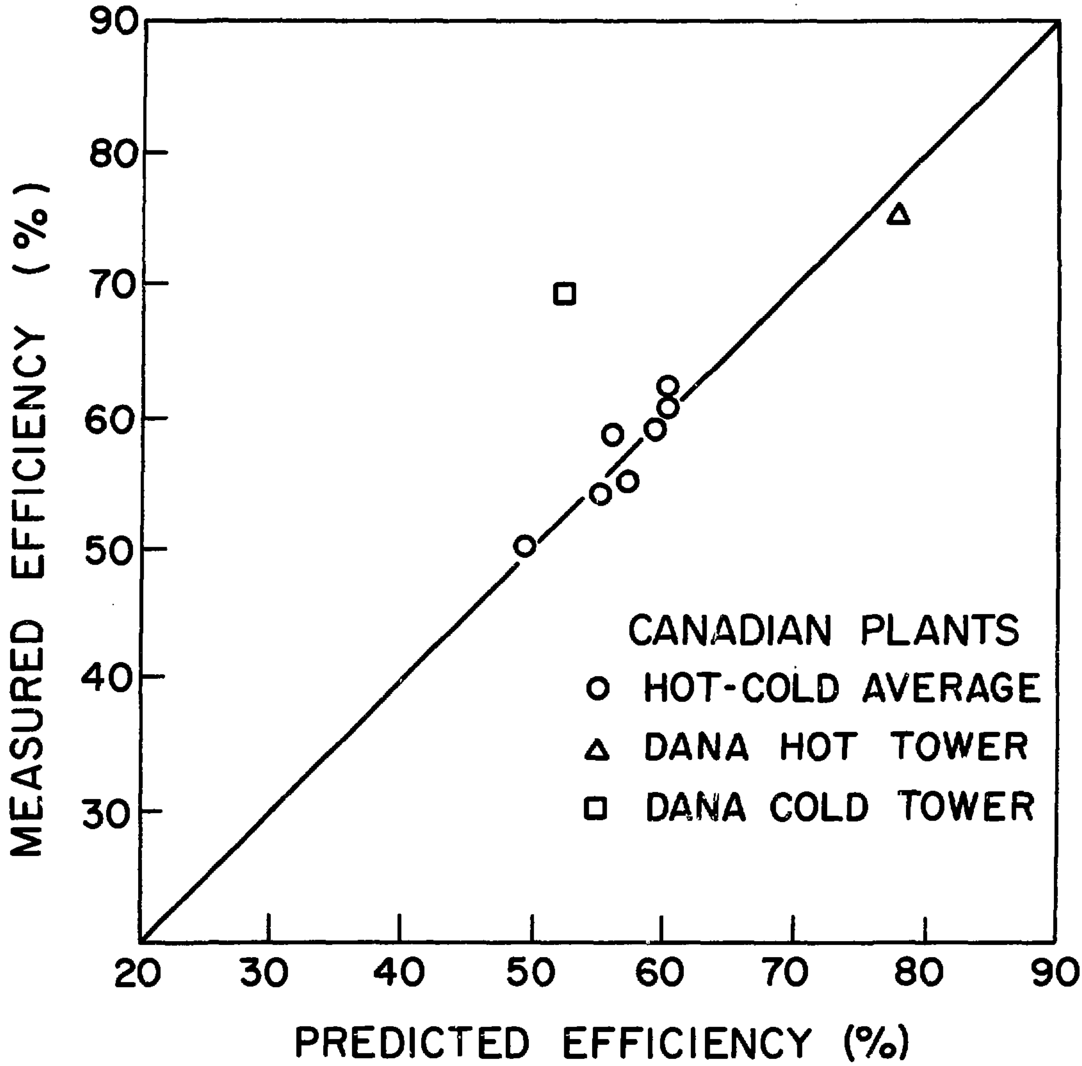
The active area on the tray is the surface on which gas and liquid are contacted. It is given by the area of the tower less the areas of downcomers. It is very important to establish the design of sieve tray panels that occupy the active area in terms of relative open hole area, hole diameter and distribution of liquid flow-promoting devices that will force liquid flow on the tray to follow an ideal path. Relative open hole area plays a decisive role in determining tray pressure drop and turndown capacity. Normally open hole area on GS trays is adjusted to suit the capacity of the circulating blower. Typically the total tray pressure drop is no greater than 800 Pa/tray and turndown is about 70% of design flow for 25% weeping. Hole diameter has a weak influence on hydraulic performance, but smaller holes result in higher tray efficiency for trays operating in the low gas velocity region. On the other hand, hole pluggage due to sulphur compound deposits creates more severe operation problems on smaller hole size trays than on trays with larger holes. Hole diameters are usually in the range of 0.5 to 1.5 cm, depending on the particular requirements of certain tower regions. Proper distribution of flow-promoting devices on the tray active area is of great importance to obtain maximum tray efficiency within existing hydraulic restrictions. At present tray vendors possess the technology for flow promoter design, but theoretical and experimental studies are underway at CRNL to develop a more advanced understanding of this subject (3.6.3).

3.6.4 Tray Efficiency

Tray efficiency depends on three sets of parameters; system properties, vapour and liquid loading, and tray geometry. The designer has little control over the first set but can effectively deal with the other two. A tray efficiency model has been developed at CRNL (3.6.4, 3.6.5) that is capable of accurately predicting tray efficiency for given pressure, temperature, flow conditions and tray geometry. The model takes into account effects of entrainment, weeping, gas mixing, liquid mixing in the downcomers and two-dimensional liquid flow distribution on the tray surface.

Predictions of plant tray efficiencies by the model have been in very good agreement with direct plant measurements, as shown in Fig. 3.6.3. It is interesting to note that a discrepancy was found with the cold tower efficiency of the Dana plant measured by Proctor (3.6.1), using a technique of altering the ratio of gas-to-liquid flows in the towers. This discrepancy, which is worth about 17 percentage points in tray efficiency, explains why cold tower trays in Canadian plants did not achieve design performance. Proctor had to derive tray efficiency numbers from overall tower performance under extremely pinched conditions. It is likely that his measured value for the cold tower is erroneous.

FIGURE 3.6.3 - MEASURED vs PREDICTED TRAY EFFICIENCY FOR GS PLANTS



3.6.5 Plant Tray Modifications

Great benefits from tray modifications have been realized at the heavy water plants since 1976 when more firmly based correlations on tray design began to evolve. Those changes directed at improving tray efficiency are listed in Table 3.6.1. It can be seen that the production gains were substantial.

Other tray changes involved increasing the open hole area of the trays in the top of the hot tower of BHWP E1A. This change successfully demonstrated that a higher open hole area tray reduced entrainment.

A redesign of the transfer trays in the dehumidifier sections of the first and second stages at PHHWP resulted in dramatic improvement in plant performance. Through gamma scanning these trays were recognized as a "bottleneck" to increased production because they limited flows. Analysis of the trays confirmed the problem and new trays were designed to perform a heat transfer function rather than simply a transfer function. These tray changes, along with a number of other equipment improvements, resulted in a 10% increase in production, of which a significant fraction was attributed to the tray program.

Table 3.6.1 Benefits of Plant Tray Modifications

Location	Changes	Tray Efficiency Gain	Production Gain
PHHWP Stage 1	Raise CT weir on alternate trays	1.5% points	1%
GBHWP Stage 3	Raise weirs in CT and HT	23% points	12%
GBHWP Stage 1	Raise weirs in CT Replace multipass trays with 2-pass trays in HT	11% points	2.4%
GBHWP Stage 1	Raise weir in CT Replace multipass trays with flow promoted 2-pass trays in HT	13% points	2.8%*

* if all first and second stage towers were modified, production gains would be 23.9%.

3.7 Gamma Scanning - D.A. Spagnolo, CRNL

3.7.1 Introduction

During the early years of operating the Canadian heavy water plants, design flows were not achieved because of hydraulic instability on the trays. Determining the type and location of the instability was extremely difficult because the plants were not instrumented for analysing tray performance. The large towers, high operating pressure and toxicity of H_2S deterred new tower penetrations, and this limited new instrumentation. To provide a means of detecting tray damage and studying tray operation without penetrating the tower walls, the gamma scanning technique was refined for large diameter towers by CRNL (3.7.1, 3.7.2). Some earlier scanning had been done on the smaller SRP towers in the USA by Dupont (3.7.3).

Gamma scanning has since developed to the stage where it is routinely used at all Canadian heavy water plants for maintenance planning, troubleshooting, and performance evaluation.

Ontario Hydro operates two scanning units at the BHWP. NSRF uses a portable scanning unit owned by AECL-CC and conducts scans for PHHWP and GBHWP on a contract basis. CRNL provides the development and maintenance of the equipment for the heavy water industry and operates a portable scanning unit for its GS pilot plant.

Information on gamma scanning is exchanged and discussed through the Gamma Scanning Working Party, which periodically meets and is made up of representatives from the heavy water plants, scanning and development groups.

3.7.2 Equipment

When gamma rays penetrate a vessel, some rays are absorbed or deflected while others pass through. The fraction that penetrates depends on the strength of the radiation source, and the density and thickness of the intervening materials. If the source strength and vessel thickness remain unchanged, density differences within the vessel can be related to the number of rays that penetrate. This ability to detect density differences is the basis for the gamma scanning technique.

Scanning involves the synchronous raising (or lowering) of a gamma source (normally Co-60) and a scintillation detector on opposite sides of the vessel as illustrated in Fig. 3.7.1. The equipment consists of a gamma source, a detector, collimators, elevating devices, electronics to analyse the detected signal, and some type of information output display. The latter can range from a simple strip chart recorder to a sophisticated on-line computer. All equipment is commercially available except for the holding and elevating devices, which were designed and developed by CRNL.

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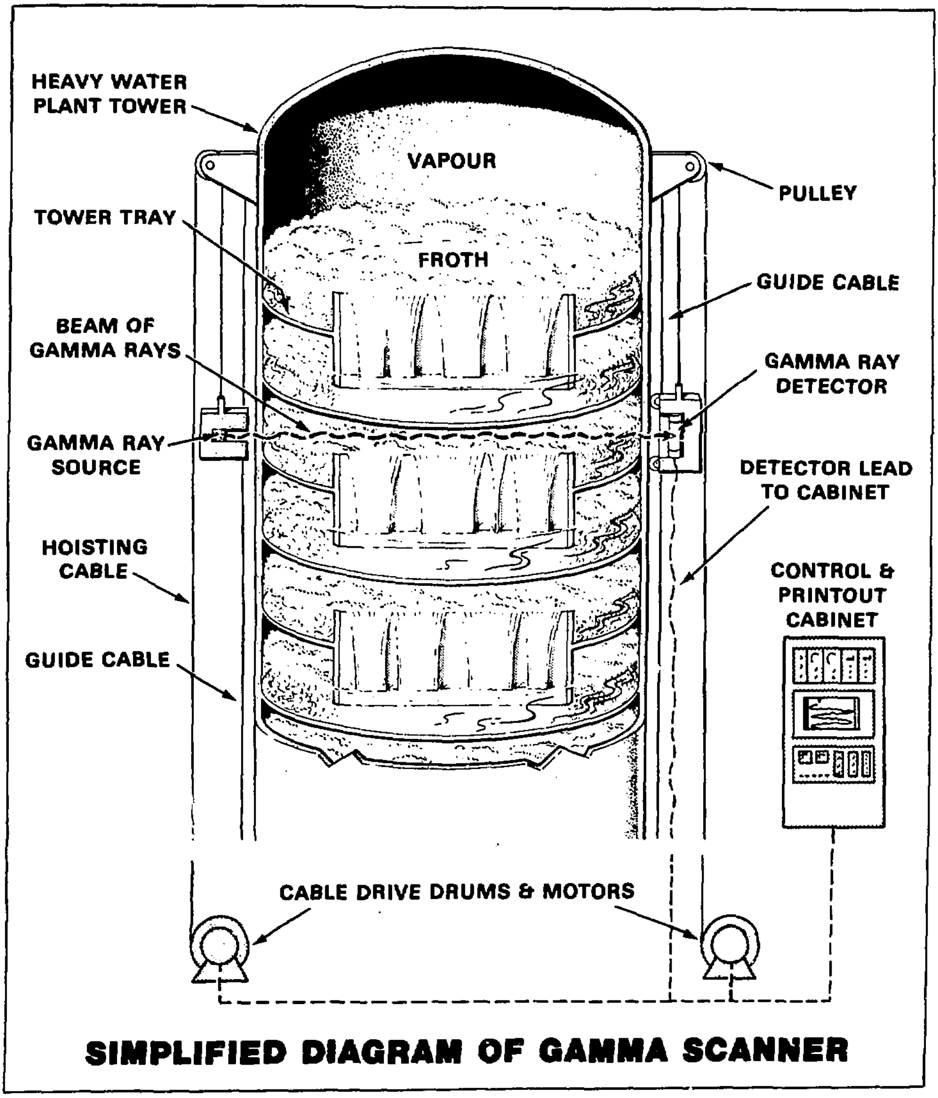

Figure 3.7.1

Simplified Diagram of Gamma Scanner

3.7.3 Applications

3.7.3.1 Tray Hydraulics

Gamma scanning can provide valuable hydraulic information on the performance of sieve trays. Froth height, liquid holdup and froth density are readily attainable, and can be applied to:

- evaluate the effectiveness of tray modifications, which in turn is used to develop tray models and optimize tray design,

- determine the effects of changes in operating conditions on tray performance,

- evaluate chemical process changes,

- establish the location and mechanism of tower loading and instability, and

- detect changes in tray operation arising from foaming or mechanical damage.

Scanning is extensively used to measure froth heights on sieve trays. From such data, outlet weir heights have been either reduced to improve hydraulic stability or increased to improve mass transfer efficiency. For example, scanning established that the cause for low tray efficiency in a particular tower at Glace Bay HWP was due to low froth height and liquid holdup on the trays. Raising the weirs to increase froth height and liquid holdup increased tray efficiency by 20 percentage points.

Similarly, scanning has been used to evaluate the influence of hole size and open hole area of sieve trays. Here several trays in a section of a tower at the Bruce HWP were changed and "before" and "after" scans were compared. In the studies of open hole area, scanning was used to determine the upper flow limits for the various trays.

Horizontal scanning involves the incremental movement of the detector circumferentially around part of the tower while keeping the position of the source fixed. Such scanning at the Bruce HWP revealed that froth heights on side downcomer trays were more uniform than on center downcomer trays. The lower hydraulic gradient on SDC trays was interpreted to mean a more uniform flow distribution and thus higher tray efficiency. The scanning confirmed the need for new types of directional flow and entrance promoters for CDC trays.

A scan of a typical operating tower consists of a series of peaks and valleys as shown in Fig. 3.7.2. The peaks of high gamma transmission represents the low density vapour phase. The valleys of low transmission are caused by the dense froth on the tray decks and by the metal trays and tray supports. Irregularities in scan patterns are usually evidence of internal structural damage. Broken trays do not support their normal levels of water and froth and abnormal tray spacing is usually indicative

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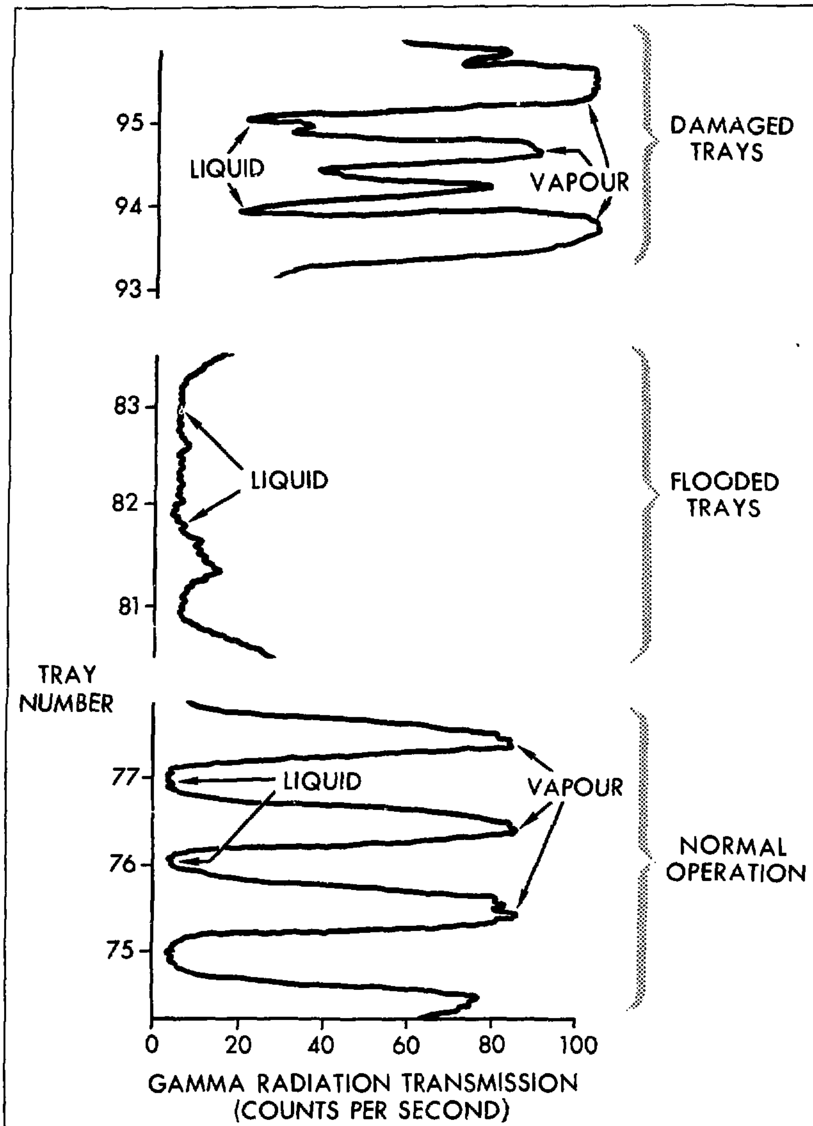


TYPICAL GAMMA SCAN RECORDS SHOWING NORMAL & ABNORMAL CONDITIONS IN AN OPERATING TOWER

Figure 3.7.2

of displaced trays. Knowing the location of damage and the number of trays involved prior to a tower shutdown is important to allow adequate time to order materials and to schedule the shutdown.

Scanning has also been successfully used to locate tray loading instabilities. The absence of peaks on a tower scan (Fig. 3.7.2) indicates the absence of a vapour space between trays and thus, the presence of flooded trays.

Scanning has been used to evaluate new antifoams during plant trials by determining the effect of the antifoam and its concentrations on tray froth heights.

3.7.3.2 Tray Blockage

Iron sulphide, because of its inverse solubility with temperature, can deposit on sieve trays in hot sections of the towers. The iron sulphide crystallizes around the tray perforations, causing gradual reduction in the open hole area of the tray. A qualitative means of monitoring the progress of this fouling during plant operation using gamma scanning was developed to more efficiently schedule tower shutdowns for tray cleaning.

Scanning provides a profile of froth height against tray number as shown in Fig. 3.7.3. A deposition gradient occurs with highest deposition occurring on the top tray of the hot tower. As deposition progresses with time the slope of the froth height versus tray number profile changes. The profiles illustrated in Fig. 3.7.3 are for constant operating conditions. The froth heights can be qualitatively related to actual plug gauge measurements taken during plant shutdown.

3.7.3.3 Heat Exchanger Fouling

The vertical process steam heat exchangers in the humidification circuit is another place where iron deposition can be severe. Fouling of these exchangers reduces heat transfer efficiency and makes cleaning necessary. Monitoring fouling during plant operation with gamma scanning enables more efficient shutdown scheduling for cleaning. Fouling can be monitored in two ways:

1) qualitatively by following the decrease in condensate level at the bottom of the exchanger, and

2) quantitatively by following the actual deposit thickness in the exchanger tubes.

Thus a vertical scan of the exchanger yields a gamma intensity profile (Fig. 3.7.4) which for a clean exchanger is relatively uniform from top to bottom and has a relatively high condensate level. For a fouled exchanger the gamma intensity decreases with height, indicating an increase in deposit thickness. Also, the condensate level decreases to provide a larger heat transfer surface.

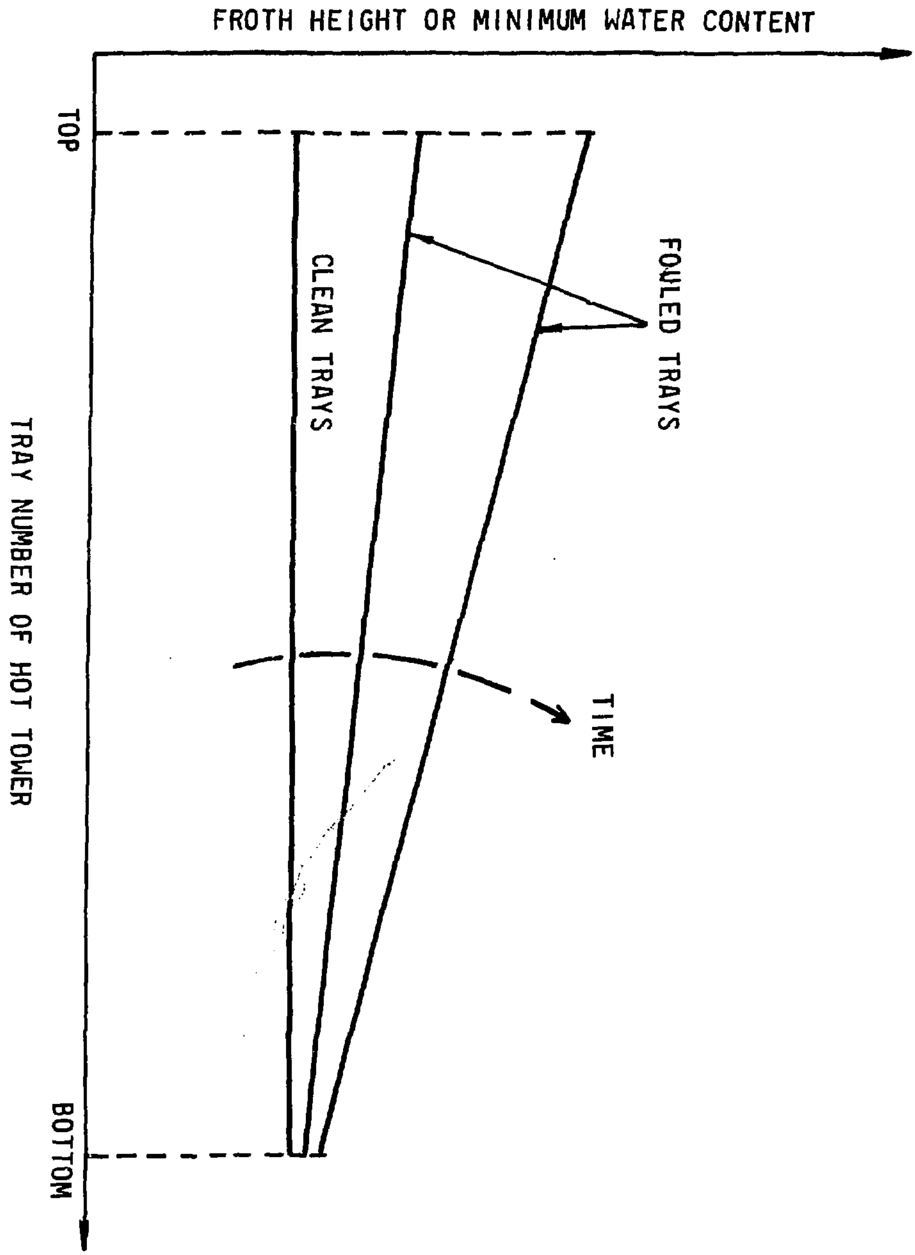
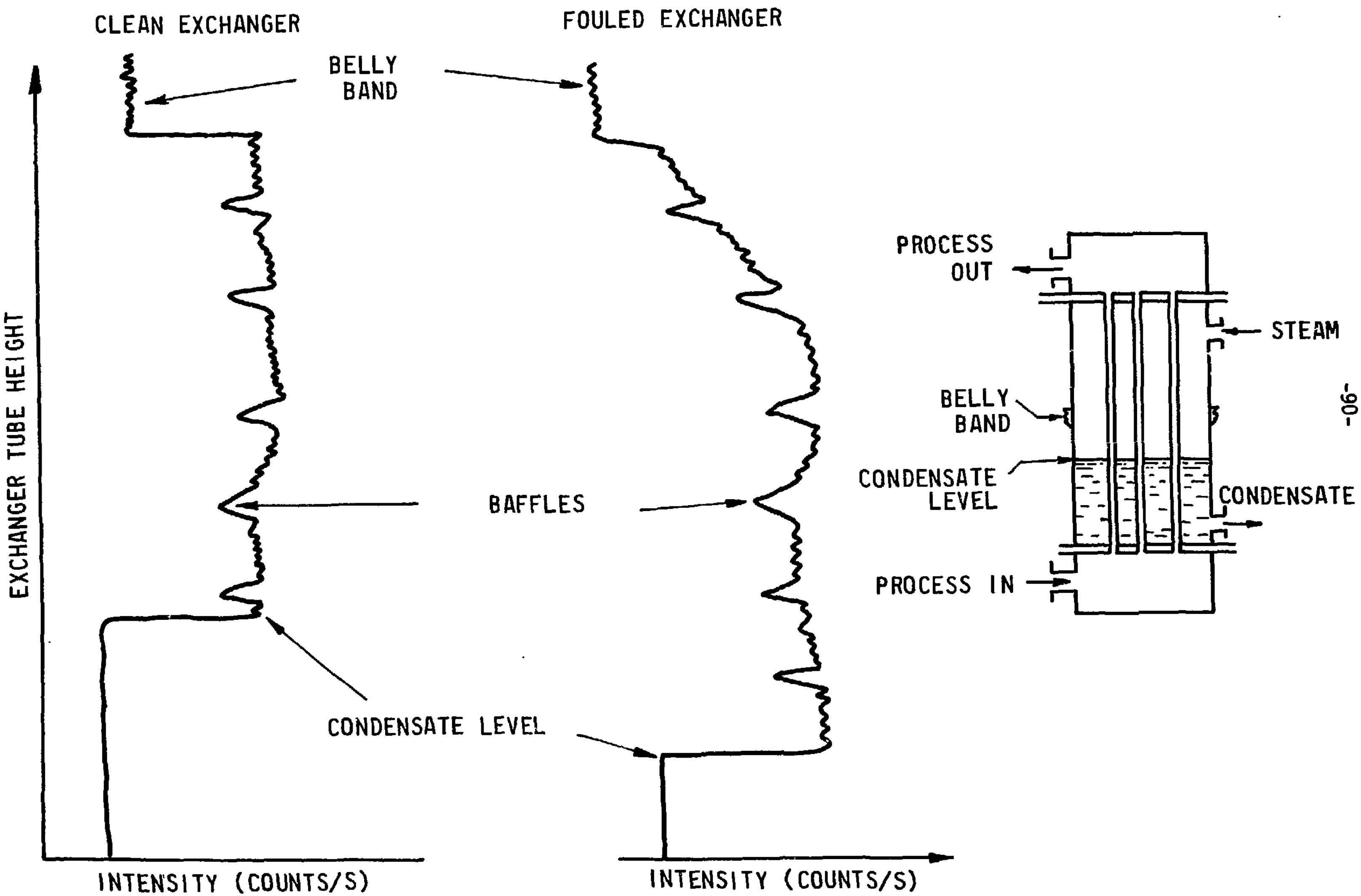


FIGURE 3.7.3: TRAY DEPOSITION PROFILE

FIGURE 3.7.4: GAMMA SCAN PROFILE OF A STEAM HEAT EXCHANGER



From gamma measurements of a fouled exchanger and its reference clean scan, the thickness of the deposit can be calculated. These calculated thicknesses have agreed well with those measured directly with plug gauging during a shutdown.

3.7.3.4 Liquid Level

In addition to measuring steam condensate levels in vertical heat exchangers, gamma scanning has been used to measure the level of liquid H_2S in storage tanks when level instruments have failed. Scanning has also successfully diagnosed poor operation of packed absorber towers by identifying areas where flooding has occurred. Scanning has also detected sulphur/water interface levels in condenser receivers and knock-out drums.

3.8 Water Distillation - M.R. Galley, AECL-Chemical Company

3.8.1 Introduction

The GS process plants in Canada were all designed to use water distillation for upgrading the product from the 10% to 25% range to reactor grade. The water distillation (DW) units at the four Canadian plants are each quite different in design and configuration. The DW unit at Port Hawkesbury was supplied by Sulzer and consists of two columns, one packed with Sulzer BX packing and the other containing very small Dixon rings packed into many parallel vertical support tubes. All packing materials are phosphor bronze with an adherent black copper oxide coating to promote good wetting. Early operating data for this DW unit was not recorded because its operation was overshadowed by problems in the GS units, but one or more attempts at packing surface regeneration were made in the early 1970s. By 1975 it was apparent that loss of copper oxide coating, or contamination by materials that made the oxide non-wetting, was causing a severe loss of theoretical plates. At about this time CRNL began a program of testing various proprietary DW packing materials to determine their capabilities and to find means of obtaining good surface wetting characteristics. It soon became clear that phosphor bronze packings worked well only if they were protected from acid conditions and contamination by oil and other organics.

3.8.2 Packing Fouling and Cleaning

The problem of cleaning and regenerating fouled packing was also investigated and procedures were recommended to the operating plants. Some procedures to re-establish the oxide coating involve the use of pure oxygen which could pose safety hazards in equipment that might be contaminated with residual organics. Alternative procedures using air have been developed but are somewhat less effective in establishing an adherent oxide with acceptable surface characteristics. More recently a different approach has been taken and this involves the use of feedwater additives which make the water wet the packing without creating a foaming problem. If this approach is successful it may be possible to use almost any convenient inert material for packing manufacture.

3.8.3 Plant Systems

When the Glace Bay plant was rehabilitated, two of the old DCL towers were converted to a DW unit. The first tower was packed with plastic Pall rings and the second tower was filled with canisters of Sulzer CY packing. The plant was commissioned with water of questionable purity and performance rapidly deteriorated. When the whole plant was shutdown for heat exchanger repairs in 1977, the DW was inspected and cleaned. The plastic Pall rings, which had a high pressure drop and were leaching organic material, were removed and replaced by phosphor bronze Mini Rings, which had been tested at CRNL. The DW unit performed at close to design conditions for a short while and then deteriorated to a plateau level, well short of design performance expectations. Subsequent tests and inspections have shown a loss of theoretical plates in both columns, due partly to loss of oxide surface. However, the substitution of Mini Rings did cure the pressure drop problem in the first column.

In the course of these packing studies in support of Glace Bay and Port Hawkesbury, CRNL initially ran tests in the upgrader column of the NRU reactor and later assembled a dedicated test facility for packing performance evaluation. Considerable precision in deuterium analysis is necessary because of the low separation factor and the restricted length of the test column but the deuterium isotopic analysis facilities at CRNL proved adequate for this purpose.

The packed column DW units at Glace Bay and Port Hawkesbury continue to operate at well below their design ratings and this situation is tolerated because production rates can be maintained by drawing product at below reactor grade. This water is then sent to CRNL for final upgrading by electrolysis. Work on new packing development has essentially ceased pending a decision on whether to continue the current mode of operation or to modify the plant DW units. New developments in hydrogen water exchange technology and the CECE process may eventually make DW systems obsolete.

The DW unit at the Bruce A heavy water plant uses sieve tray columns and has operated very well at design throughput. The only changes made were to remove outlet weirs from the trays to reduce pressure drop and increase efficiency of overall operation. The chief disadvantage of sieve tray columns in DW service is the very large inventory of heavy water resident in the unit. The Bruce B plant has a Sulzer DW unit for the F2 finishing unit. Based on feedwater treatment experience at Port Hawkesbury and Glace Bay a potassium permanganate reaction step was included in the feed treatment system to remove oil and other organic species. Although this system has provided feedwater within Sulzer specification, there is evidence that some of the copper oxide coating has been removed from the packing close to the water distributors in the first stage towers. For the F4 finishing unit ultrafiltration equipment was installed. This decision was based on a trial of an ultrafiltration unit in the F2 unit (which demonstrated oil removal to less than one ppm) and on a cost comparison with the carbon filter/potassium permanganate reactor unit.

4. ECONOMIC BENEFITS - A.R. Bancroft, CRNL

4.1 R&D Effort

Effort at the various sites expressed in professional man-years (pmy) is shown in Table 4.1. At CRNL, WNRE and OHR this was mainly engineers of various disciplines and chemists. Working with them in the laboratories was a staff of 1.2 technicians and technologists per professional and the normal construction, maintenance, analytical and other support services This effort can be very clearly identified in support of the various parts of the GS program. For some fields where expertise had been firmly established within the power reactor program, considerable benefit was derived by consultation alone and R&D projects were not required.

Table 4.1

SUMMARY OF GS PROCESS R&D EFFORT IN PROFESSIONAL MAN-YEARS AND 1981 DOLLARS

	AECL-RC		AECL-CC		AECL	OH	TOTAL EFFORT	
	CRNL	WNRE	HO	GBHWP	CONTRACTORS	BHWP	pmy	$million (1981)
1969	2						2	0.5
70	2						2	0.5
71	4						4	1.0
72	7				1		8	2.0
73	10	2			2	7	21	3.9
74	31	4			11	8	54	14.0
75	26	6			5	9	46	11.3
76	20	4	2	2	3	6	37	9.1
77	15	1	2	3	2	10	33	7.2
78	14		2	4	2	8	30	6.4
79	8		2	4	2	9	25	4.4
80	8		2	2	1	9	22	3.7
Total	147	17	10	15	29	66	284	64.0

At the heavy water plants the R&D effort cannot be so clearly identified, because some functions of the plant operating staff are to identify problems, propose and implement solutions and assess the changes. This process is closely interwoven with R&D. All three operating plants have Technical Departments that perform these functions. Bruce and Glace Bay plants have Technology Groups within these Departments whose function is longer-term problem-solving, i.e. on the time scale of months to years rather than days to months. For the purpose of this analysis only the individuals in these Technology Groups are included in Table 4.1.

In the AECL-Chemical Company Head Office only that effort that was directly associated with the R&D program and projects has been included. AECL contractor effort can be very clearly related to projects because the contracts were specific rather than general.

The important observations are 1) a rapid build-up over the period 1972 to 1974 to a total of 54 professionals, and 2) a slower decline to an effort of 22 in 1980.

The required R&D effort depends on the state of maturity of the process. During the next decade the effort is expected to decline slowly, if at all, from 1980 levels to ensure adequate support for operating plants and the continuing evolution of improvements.

For the purposes of this analysis in comparing production gains against R&D costs we can use approximate costs of $250 000 (1981 Canadian dollars) per professional man-year in an AECL R&D laboratory and $100 000 in a project office. These costs include overheads and the accompanying technical staff in the case of the laboratory. The Ontario Hydro costs are calculated on a different basis and averaged $160 000. The total cost of the effort identified in Table 4.1 is then $64 million.

4.2 Benefit Analysis

In the same way that the dividing line between R&D effort and plant trouble-shooting effort is not clearly defined, so the benefits attributable to these activities cannot always be resolved. The annual production figures given in Table 4.2 show the usual maturing period during which plant staff learn about plant equipment and process and eliminate restrictions to production. This effort concentrated on increasing 1) plant reliability, 2) process flows and 3) extraction (or depletion). The benefit of R&D support is more rapid learning and defining of solutions, which can be translated to a more rapid approach to maturity and probably to a higher mature production rate.

Table 4.2

CANADIAN HEAVY WATER PRODUCTION 1970 - 1980 (Megagrams)

	Port Hawkesbury	Bruce	Glace Bay	Annual	Total Cumulative
1970	13			13	13
71	63			63	76
72	183			183	259
73	129	281		410	669
74	294	640		934	1603
75	175	605		780	2383
76	112	800	39	951	3333
77	225	655	63	943	4277
78	282	736	176	1194	5471
79	242	638	236	1116	6587
80	321	653	249	1223	7810

The data in Table 4.2 confirm that experience at Port Hawkesbury was of considerable benefit to the nearly identical Bruce plant. (The single units at Port Hawkesbury and Glace Bay and the two at Bruce were all designed with a nominal capacity of 400 Mg/a.) Port Hawkesbury reached the 300 Mg per year rate in the fifth year, while Bruce did so in the second year. The large R&D effort during the period 1974 to 1976 was important in reaching the 1976 production rate of about 800 Mg per year and maintaining the rate over 600 Mg per year thereafter at Bruce. It was not until 1980, following major maintenance and an important tray change, that Port Hawkesbury was able to exceed the 300 Mg per year rate. It is important to remember that calendar years are arbitrary time periods that are not always a fair indication of plant performance because of the compulsory shutdowns for safety inspections. The Glace Bay plant, which is more difficult to operate because of process complexity and had poorer trays installed during construction, has steadily improved by making major improvements throughout the maturing period.

The justification of the GS R&D program was not based on a benefit/cost analysis before the program was committed. The evolution of the CANDU reactor and the electricity supply in Ontario using the CANDU reactor demanded a dependable and economical supply of heavy water. The judgment of AECL and OH managements based on many years of R&D activities in the nuclear field was that the required R&D effort was necessary for security of supply, but would also be rewarded economically. That judgment has been confirmed.

R&D spending in various industries as a function of product value varies considerably with the type of product. In the United States (1950-1974) it was above 7% for high technology industries (scientific instruments, electrical equipment, chemicals), in the range 2 to 7% for mixed technology (machinery, rubber, plastics, petroleum) and below 2% for low technology fields (glass, paper, metals, food, textiles). No target was set for R&D spending on the GS process, but in retrospect it has been 2.8% of the product value for the first decade. (The product is valued within the program at $300/kg for this analysis. The selling price depends on a number of factors and varies with time.) During 1974, which was the year of peak effort and was also before the main benefit of that effort had been realized, the spending rate was 5.0%. Although effort is still declining the average for the three year period 1978-80 was 1.3% of product value. For 1980 it was 1.0%. It will be lower during the second decade. These numbers appear to be in line with spending by others in the chemical processing industries and indicate that the criteria used by management to approve R&D spending were normal.

4.3 Project Benefits

Once new technology has been made available through an R&D program its application to a production plant must meet the financial criteria applicable at this time. The R&D costs incurred in developing the technology do not enter into this analysis because their costs have already been covered. Retrospective analysis of the benefits and costs of an R&D

program serves to test the validity of decisions and to identify means of improving future ones. However, the approval of R&D funds for future investment always depends on anticipated benefit.

For a process industry in its infancy, the benefits of an R&D program are generally reflected in increased productivity and in some instances are relatively easy to quantify. As the industry matures the benefits shift from increasing productivity to sustaining productivity. This latter benefit is difficult to quantify.

A breakdown of the demonstrated benefits and costs is listed in Table 4.3. The benefit of the overall program is more difficult to quantify than specific areas and it is currently estimated to be $240 M, at a benefit to cost ratio of 4. This is understandably lower than the ratios for specific activities because it includes some of the related services, such as analytical chemistry, materials development, mechanical equipment development and gamma-scanning for which there was R&D spending. The benefits for specific activities show a substantial benefit for R&D spending and clearly justify the selected R&D program. Since there is generally several years time lag between spending R&D funds and verifying its benefit, some of the benefits anticipated from the spending during the past decade will continue to accrue well into the next decade. This will improve the benefit to cost ratio for the program.

Table 4.3

GS PROCESS R&D BENEFITS

Activity	Benefit M$	Cost M$	Benefit/ Cost
Process Simulation	96	8	12
Sieve Trays	42	7	6
Antifoam	20	1	20
Entire Program	240	64	4

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