ADVANCES IN THE FLUOROCARBON PROCESS FOR DECONTAMINATION OF NUCLEAR FACILITY OFF-GAS

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Oak Ridge Gaseous Diffusion Plant*
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Oak Ridge, Tennessee

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INTRODUCTION

The Nuclear Division of Union Carbide is responsible for the development of the fluorocarbon-based selective absorption process for removing noble gas fission products, carbon-14, and other radioactive contaminants from the gaseous wastes of nuclear facilities. In order to accomplish the duel objectives of component removal and subsequent concentration, the process utilizes three operations: absorption, fractional stripping, and final stripping. Each of these performs a separation by exploiting the solubility differences between the various off-gas components in the process solvent, dichlorodifluoromethane (R-12). The performance and reliability of the process have been demonstrated on an engineering scale with 10 years of pilot plant operation at the Oak Ridge Gaseous Diffusion Plant (ORGDP) which included extended testing with ^{85}Kr, ^{133}Xe, and ^{131}I. Removal efficiencies of greater than 99.99% for Xe, CO_2, I_2, and CH_3I, greater than 99.9% for Kr and H_2O and greater than 99% for NO_2 and N_2O have been experimentally obtained. With a feed stream containing 150 ppm of noble gas, a 97% noble gas product has been achieved. In addition to demonstrating the required removal efficiencies, the process has shown a remarkable tolerance for many of the normally troublesome off-gas components and does not rely upon elaborate feed pre-treatment steps. Recent work has led to a major flow scheme simplification, reducing the three-column process to a single patented column. A third generation pilot plant facility employing this new concept has successfully undergone initial testing

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this last year at ORGDP.

BACKGROUND

Throughout its history, the fluorocarbon development effort has addressed off-gas applications in almost every aspect of the nuclear fuel cycle. Steinberg[1] originally suggested using R-12 as a solvent in a three-column process to selectively absorb Kr and Xe from the gaseous wastes of a reprocessing plant in 1959. In 1966, a pilot plant was constructed and a development effort was initiated at ORGDP to establish the general feasibility of the fluorocarbon process. At that time, the work was aimed at the development of a mobile processing system which could be transported to the site of a hypothetical reactor within 24 hours of a fuel failure accident and recover the noble gases and other volatile radionuclides released to the containment vessel. As envisioned, all of the recovery equipment was to be situated in a series of trailer trucks[2]. Unfortunately, with respect to the Three Mile Island incident, this work did not proceed past the conceptual design stage.

In 1970 the program emphasis shifted to the routine cleanup of LWR off-gases[3], and the fluorocarbon process was subsequently offered commercially for LWR application[4].

Based on the demonstrated operability and performance of the ORGDP pilot plant, process safety considerations, and in particular, the lack of any required feed pre-treatment, the fluorocarbon process was adapted for reprocessing plant applications in 1971. A second generation pilot plant facility was built at ORGDP in 1972 which offered greater flexibility and the more sophisticated analytical equipment necessary for detailed component analysis[5]. This facility demonstrated that in addition to providing Kr and Xe removal, the fluorocarbon process could effectively be utilized to contain carbon-14 as CO_2, various nitrogen oxides, elemental and organic iodine, and water. Rigorous process models and scale-up studies[6,7,8] were completed to allow the confident design and optimization of a full-scale facility. These works laid the groundwork for the construction of the single column process in 1978.

The concept of the fluorocarbon process as a mobile emergency reactor off-gas decontamination system has recently been revived in the wake of the Three Mile Island incident and is undergoing review by responsible persons in the industry. It would be possible to have a mobile unit ready for deployment within three to four years.

PROCESS BASIS

Fluorocarbon solvents have been identified as a valuable and somewhat unique group of solvents unusually suited for separating a number of industrially important components from various gas mixtures[9,10]. Steinberg selected R-12 for noble gas removal primarily because of its capacity, separation factor, and thermal and radiation stability, as well as process safety and economic features[1]. The physical properties of R-12 are well known. The basic thermodynamic properties are detailed by Mr. Harness, et al.[11]

Distribution coefficients for several of the off-gas components of interest are shown in Figure 1. A substantial amount of equilibrium data now exists for krypton and xenon in R-12 solution. The initial work was performed by Steinberg at Brookhaven National Laboratory. Later work was reported from the University of Tokyo by Yamamoto and Takeda[12]. The most recent data are given by Shaffer at ORNL[13]. Merriman utilized several techniques based on Hildebrand's regular solution theory to estimate krypton and xenon equilibrium coefficients[14]. All investigators show good agreement.

Toth, et al.,[15] recently completed a laboratory study to define the behavior of other nuclear fuel reprocessing plant off-gas components such as CO_2, NO_2, I_2, and CH_3I. While I_2 was found to be fairly soluble in R-12, CH_3I, NO_2, and CO_2 were found to be totally miscible in the temperature range of interest. Distribution coefficients were also determined for these species. Beyond this work, some estimated solubility relationships have also been given[14].

PROCESS DESCRIPTION

Figure 2 is a schematic of the selective absorption process as it was originally conceived. The main separation of radioactive contaminants from the bulk gas is effected in the absorber. The intermediate or fractional stripper serves to remove the coabsorbed carrier gas from the solvent, thereby enriching the remaining dissolved gas in the more soluble components. The final stripper removes all the remaining gas from the process solvent for collection and regenerates the solvent for recycle back to the absorber. The absorption step is carried out in a packed column only, while both stripping operations are performed in packed columns with reboilers and overhead condensers. In addition, the intermediate stripper includes a flash drum. Typically, the absorber is operated at 100 psig, the intermediate stripper at 50 psig, and the final stripper at about 18 psig. Support equipment items for the basic process include a feed gas heat exchanger, process gas compressor, solvent cooler, storage tanks, and several refrigeration compressors. If the feed gas contains significant quantities of high boiling

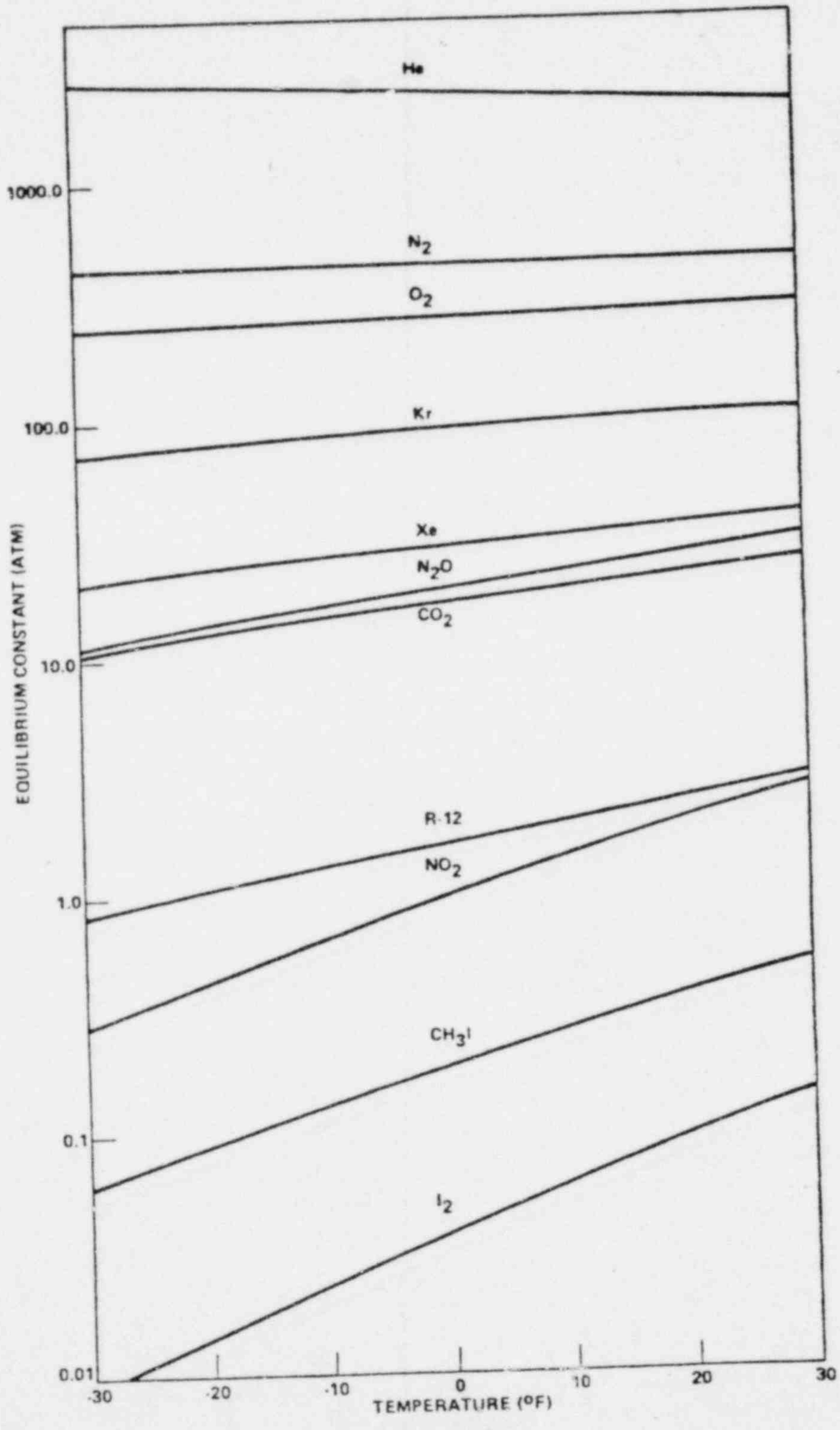


Figure 1
EQUILIBRIUM DISTRIBUTION COEFFICIENTS FOR VARIOUS FEED GAS COMPONENTS IN R-12

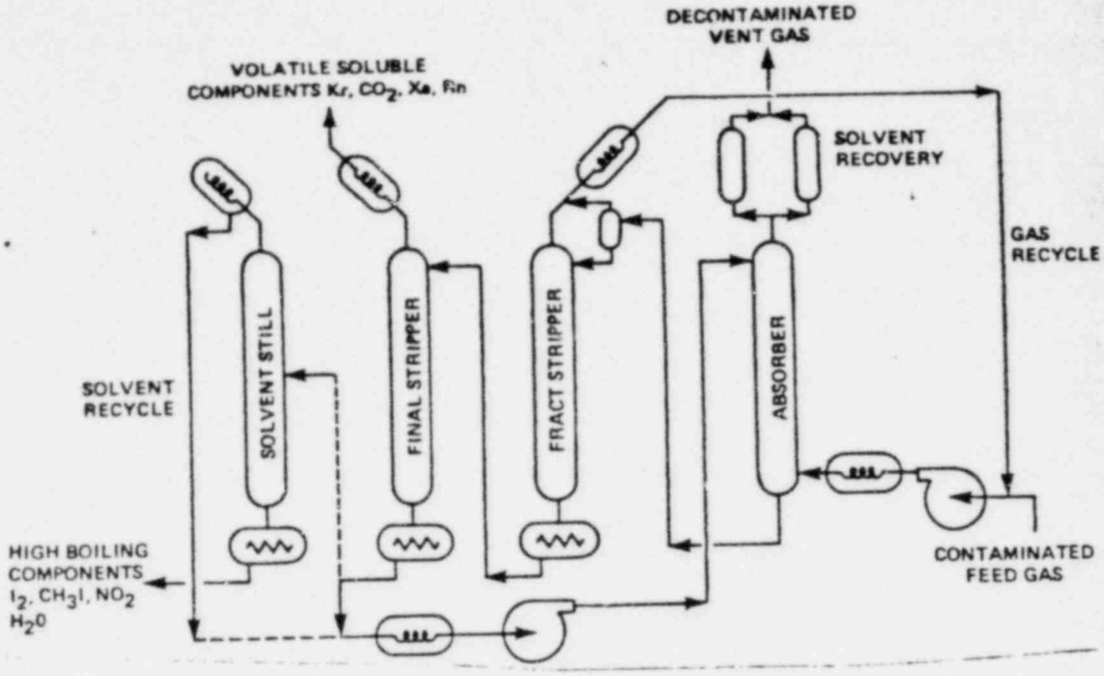


Figure 2
SCHEMATIC OF THREE-COLUMN SELECTIVE ABSORPTION PROCESS

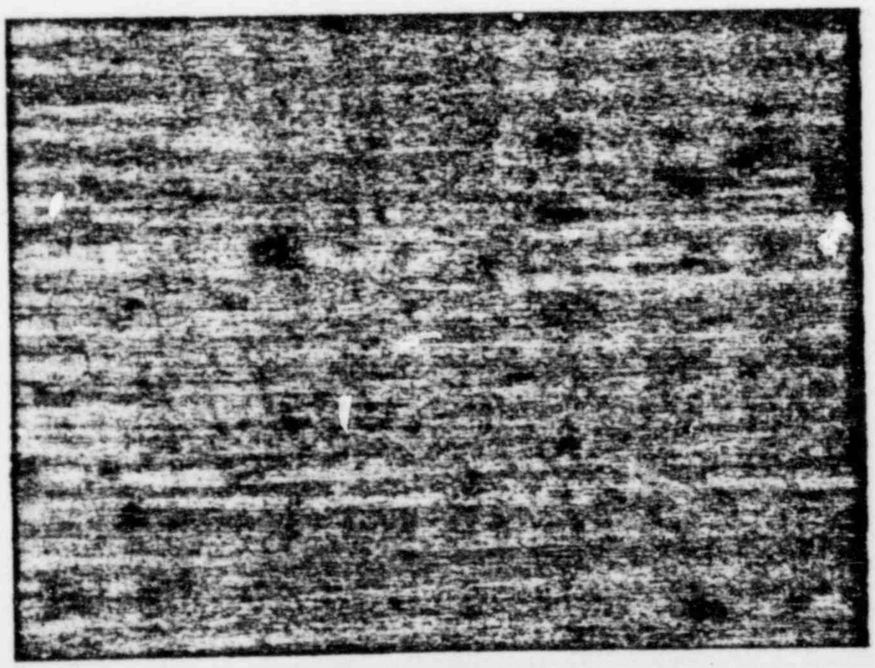
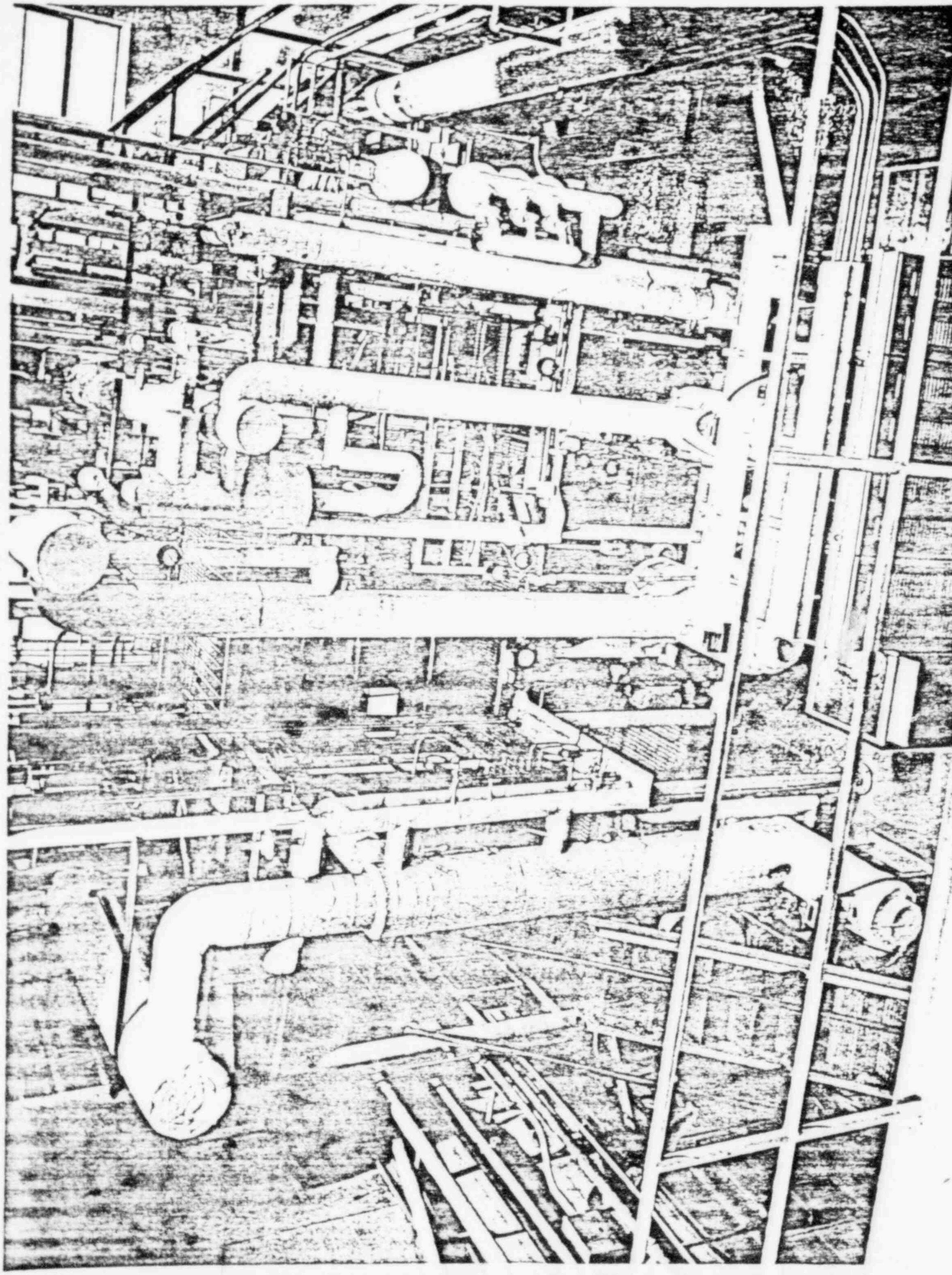


Figure 3
OVERVIEW OF ORGDP THREE-COLUMN PILOT PLANT



components such as H_2O, I_2, CH_3I, or NO_2, a solvent purification still is available as an in-line option to prevent these materials from accumulating in the recirculating solvent. A solvent recovery system is necessary to remove solvent vapor from the process off-gas. Figure 3 is a photograph of the second generation ORGDP pilot plant. Detailed engineering drawings and descriptions of this facility are available elsewhere[16].

In the course of operation and analysis of this facility, a soluble gas peak was observed in the fractional stripper. It was found that this phenomenon, caused by gross internal condensation of the upflowing stripping vapor[6], could be controlled and the magnitude of the peak could be increased dramatically. It became apparent that if sufficient stripping stages were provided below the condensation zone, the final stripper could be eliminated with the product being collected as a side-stream. Furthermore, it also seemed feasible to place the intermediate stripper directly below the absorber and operate the entire assembly at a common pressure. Subsequently, a column was designed that combined the three functional steps of absorption, fractional stripping, and final stripping into one continuous contactor[17]. Figure 4 is a schematic of this piece of equipment. Decontaminated off-gas flows from the top of the combination column and regenerated solvent is pulled from the bottom. The fission product gases are collected as a side-stream. The combination column requires substantially less equipment and control instrumentation than the conventional flow sheet, and because of its simplicity, it offers numerous operational, reliability, and economic advantages. Due to the great potential and design uncertainties, a combination column was built and installed at ORGDP for evaluation. Figure 5 is a photograph of the column taken during construction. The column is approximately 24 feet tall and has the same flow capacity as the three-column development facility. The absorption and intermediate sections are 3 inches in diameter, while the final stripper section has a diameter of 6 inches. High efficiency wire mesh packing is used throughout. Pilot plant tests have shown that scale-up on the column area is direct with this packing if well designed gas and liquid distributors are employed[7]. Hence, larger equipment utilizing the same packing material can be designed with confidence.

The combination column has been undergoing performance evaluation for almost 1 year. These tests not only established the overall feasibility of the concept, but showed conclusively that the combination column can perform essentially as well as the three-column process. On the basis of a one-to-one comparison of the two options, the combination column has recently been selected as the preferred version for future applications.

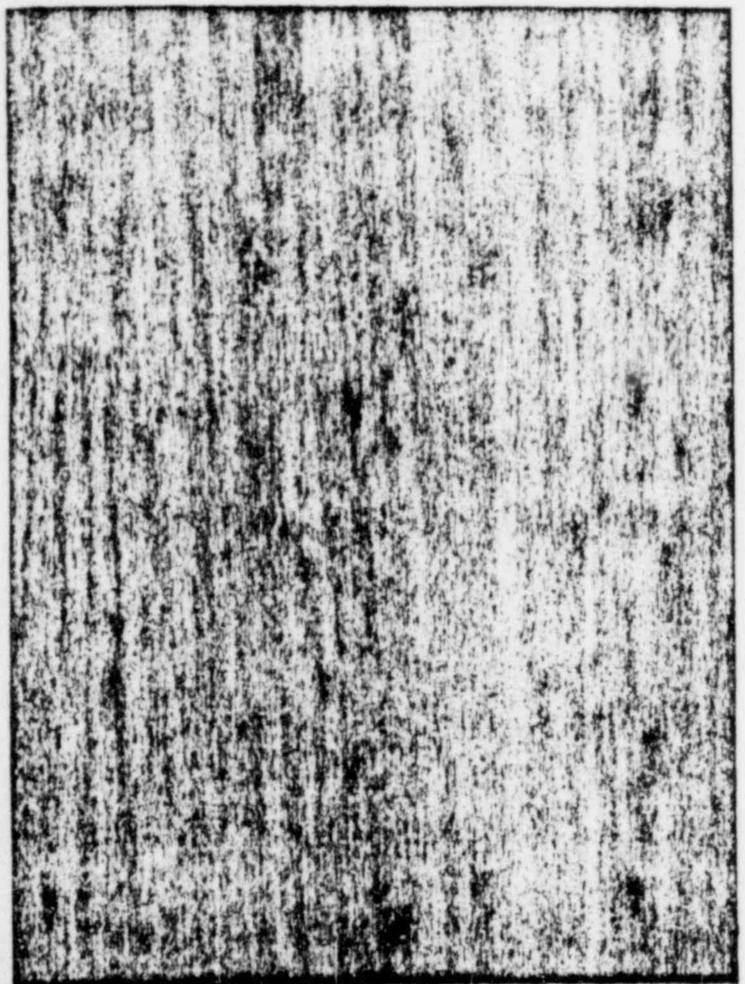


Figure 5
ORGDP SINGLE-COLUMN PILOT FACILITY

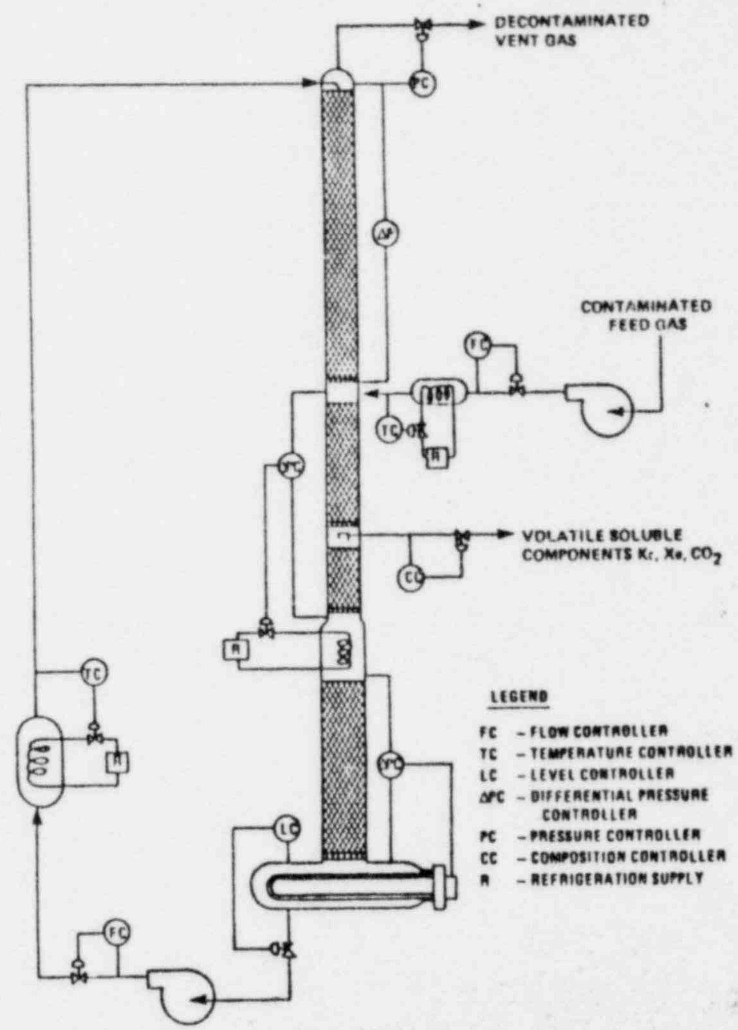
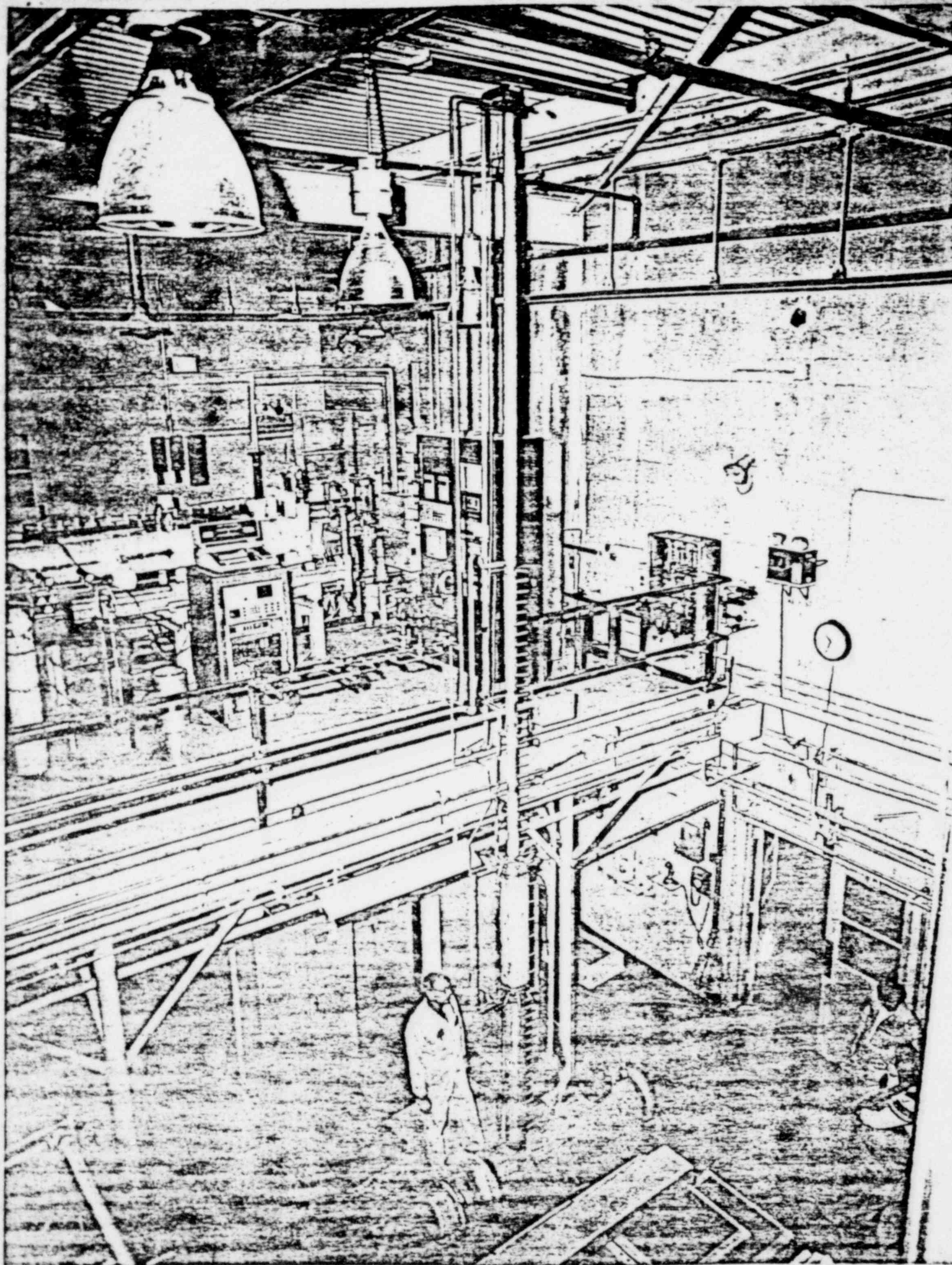


Figure 4
SCHEMATIC OF SINGLE-COLUMN SELECTIVE
ABSORPTION PROCESS



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