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MASTER

ENGINEERING DEVELOPMENT OF
AN ABSORPTION PROCESS FOR
THE CONCENTRATION AND COLLECTION OF
KRYPTON AND XENON
THIRD SUMMARY PROGRESS REPORT
JANUARY THROUGH JUNE, 1968

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UNION CARBIDE CORPORATION
NUCLEAR DIVISION

Operating the

OAK RIDGE GASEOUS DIFFUSION PLANT • OAK RIDGE NATIONAL LABORATORY
OAK RIDGE Y-12 PLANT • PADUCAH GASEOUS DIFFUSION PLANT

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UNION CARBIDE CORPORATION
NUCLEAR DIVISION
Oak Ridge Gaseous Diffusion Plant
Oak Ridge, Tennessee

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A B S T R A C T

A continuous absorption process for the separation of krypton and xenon from contaminated gas streams is being investigated in development studies at the Oak Ridge Gaseous Diffusion Plant. In this process, krypton and xenon are preferentially removed from an incoming gas stream by selective dissolution in a fluorocarbon solvent, such as refrigerant-12. The liquid stream is then subjected to a series of fractionation operations which yield a product gas stream, rich in the noble gases, and an essentially pure solvent stream, for recycle. The major part of the ORGDP program, i.e., pilot plant testing, is supplemented by conceptual plant design and optimization studies. During this report period, installation of the pilot plant equipment items was completed, and shakedown tests, using refrigerant-11 as an alternative solvent, were begun. Preliminary data from these tests have been encouraging. Conceptual design studies were limited to a literature survey for data related to the radiolytic decomposition of the process solvent. Work on the assembly of a computer code package for use in the optimization studies was completed, with incorporation of sizing and cost estimating routines into the material balance program.

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ENGINEERING DEVELOPMENT OF AN ABSORPTION PROCESS
FOR THE CONCENTRATION AND COLLECTION OF KRYPTON AND XENON
THIRD SUMMARY PROGRESS REPORT
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The Oak Ridge Gaseous Diffusion Plant is engaged in development studies aimed at investigating selective absorption as a technique for continuously removing fission product krypton and xenon from contaminated air streams. Such cleaning of nuclear process gases may be necessary in a variety of situations, including reactor accident follow-up, fuel reprocessing, and cover gas treatment for reactors using vented fuel elements.

Since krypton and xenon are much more soluble than argon, oxygen, and nitrogen in liquid fluorocarbon solvents, such as refrigerant-12, gas-liquid absorption is a promising unit operation for the collection of these fission gases. The appeal of an absorption scheme is increased because the process can readily be made continuous, utilizing only conventional gas-liquid contacting operations. Incoming, contaminated gas can be fed to an absorption column, which is operated at a relatively low temperature and high pressure and which contains a sufficient number of equilibrium stages to reduce the gas phase krypton and xenon concentrations to the low levels required for safe atmospheric disposal. The exiting solvent stream, containing dissolved krypton and xenon, can then be routed to one or more higher temperature-lower pressure stripping columns, where the dissolved gases can be further enriched in krypton and xenon and then ultimately desorbed to yield a concentrated gas product stream, for storage or secondary processing, and an essentially pure liquid stream, for recycle to the absorber.

The ORGDP noble gas program is divided into three main areas. The most important of these is pilot plant testing, which is aimed both at demonstrating overall process performance and feasibility and at establishing the mass transfer and other engineering parameters required for the confident design of plant-scale systems. For purposes of data collection, the pilot plant is sized to accommodate feed gas flows on the order of 15 scfm at absorber pressures up to 40 atm and at temperatures as low as minus 100°F, even though such extreme conditions do not appear necessary for most gas cleaning applications. The piping is such that a variety of flow schemes can be tested, ranging from a simple two-column process, involving an absorber and one stripping column, to a more complicated combination of the absorber column, two single-stage flash units, and two strippers.

Supplementing the pilot plant efforts are conceptual design studies, directed toward the preparation of detailed equipment layouts and cost estimates for plants designed to meet specific krypton-xenon decontamination requirements. Also, process optimization studies are being used to guide both the pilot plant testing and the conceptual design work by supplying estimates of the system operating parameters which lead to the lowest cost plants.

Progress made in each of these areas during the last half of FY-1968 is discussed in the following sections. For a review of previous work on this project, reference can be made to the two earlier progress reports [2,3].

SUMMARY

During this report period, the major emphasis was placed on completing the construction, procurement, and installation of the pilot plant equipment items. Installation was completed during the first 4 months of this period, and leak checking, shakedown operations, and preliminary testing using refrigerant-11 were begun shortly thereafter. From a hardware standpoint, system operation has so far been satisfactory, with only a few modifications indicated. Similarly, from an overall process standpoint, performance has been encouraging, with substantial concentration and enrichment of krypton even with an alternative solvent and at relatively high absorber temperatures.

Work on the conceptual design of plant-scale absorption systems was limited to a literature survey aimed at gathering data related to the radiolytic decomposition of the process solvent. These data will be used to estimate solvent degradation rates for a variety of processing situations.

All of the basic computer programming work required for the optimization studies has been completed. The code package now consists of a mathematical model of the absorption process, for making material balance calculations, with auxiliary routines for equipment sizing and cost estimating.

PROJECT DEFINITION

There were no changes in basic project orientation during this report period. As noted in the previous progress report, both the experimental and study efforts are being conducted from a relatively broad base so that the results will be applicable to a variety of krypton-xenon removal problems.

PILOT PLANT STUDIES

M. J. Stephenson, L. W. Anderson, D. L. Burkett

A schematic pilot plant flow diagram is shown in figure 1. As described in the previous reports, the feed gas is compressed to the absorber column operating pressure, passed through a desiccant for moisture removal, and then cooled to the desired column temperature. This stream is next introduced at the bottom of the packed column and is contacted with the down-flowing liquid solvent stream. Gas leaving the top of the absorber,

Figure 1
 KRYPTON-XENON ABSORPTION PROCESS PILOT PLANT
 SCHEMATIC FLOW DIAGRAM

depleted in krypton and xenon, is used as a coolant for the incoming feed gas before being recycled or, perhaps, vented. Similarly, the liquid effluent from the bottom of the column, containing absorbed gas enriched in krypton and xenon, is first heated by the inlet solvent and is then fed, after some further warming, to a higher temperature, lower pressure fractionation system consisting of a flash unit, a packed column, a reboiler, and primary and secondary condensers. Use of cold exiting process streams to chill incoming feed streams allows a considerable reduction in refrigeration requirements and, consequently, in processing costs. In the fractionator, a portion of the absorbed nitrogen and oxygen is preferentially desorbed to concentrate the noble gases contained in the liquid phase further; the resulting gas stream, containing recycle krypton and xenon, in addition to argon, oxygen, and nitrogen, is returned to the bottom of the absorber. Liquid exiting from the fractionator is routed to a stripping system, again involving a flash unit, a packed column, a reboiler, and condensers. The stripper is operated at a still lower pressure to facilitate liquid transfer and gas desorption. In the pilot plant, the product gas is recycled to conserve krypton. As noted, the pilot plant design is flexible enough not only to permit considerable latitude in the selection of operating parameters but also to accommodate a variety of equipment arrangements and flow patterns.

Flow Sheet Development

No flow sheet changes were made during this report period.

Equipment Design

Design of the pilot plant equipment was completed prior to this report period and is discussed in the two earlier progress reports.

Construction, Procurement, and Installation

All of the original equipment items for the pilot plant, including the gas compressor and the liquid pump, and the initially required instrumentation have now been installed. The shakedown tests, discussed in the following section, have, however, indicated the need for the addition of (a) molecular sieve traps, for water removal, to the solvent charge portion of the system; and (b) more heat transfer surface area, for process gas cooling, to the absorber gas feed line. The desiccant traps have been fabricated and installed, and the heat exchangers have been procured, with installation of these units planned as soon as the preliminary tests are completed. Also, final insulation of the pilot plant equipment was begun and is now over 75% complete.

Operation

Prior to initiating pilot plant operations, a few bench-scale tests were made to check the pressure drop characteristics of the packing employed in the pilot plant columns*. The column sizing and specification of flow rates had been based largely on extrapolated vendor data regarding packing throughput capabilities, and it was felt desirable to confirm these data prior to pilot plant startup in order to minimize the chances for inadvertent flooding in the initial runs. Using a 3-inch-diameter glass column, packed to a height of 2.5 feet, several tests were made with countercurrent streams of air and water at flow rates covering the ranges expected in pilot plant operations. In general, it was found that the extrapolations of the manufacturer's pressure drop data, which were apparently collected on organic distillation systems at comparatively low L/G ratios, had been conservative and tended to predict higher pressure drops and lower flooding flows than were actually observed in the test absorption system. Thus, if the refrigerant-air system behaves similarly, there should be no difficulty in operating the pilot plant over the planned flow ranges.

The first phase of the pilot plant shakedown operations consisted of leak checking and testing of the gas compressor and the liquid pump. Some valve repair was necessary to permit compressor operation at the desired maximum discharge pressure of 600 psig. Also, several small leaks, mostly through sampling valve seats and column joints, were detected and eliminated.

The second phase of the shakedown tests, i.e., operation with refrigerant-11 to check system hydraulics, was also begun during this report period. It was decided to substitute refrigerant-11 for refrigerant-12 during these preliminary tests because the comparatively high boiling point of refrigerant-11, 74.8°F, permitted operation without final insulation, thus facilitating equipment and piping modifications. Also, as will be noted, refrigerant-11 is, itself, being considered as a potential process solvent, so there was interest in collecting preliminary performance data for this material.

A summary of data obtained during the first test series is given in table I. Although the system probably was not operated at the optimum conditions for a refrigerant-11 based process, and even though the operations were not always smooth because of surges, etc, normally encountered in starting up a new system, the results were, nevertheless, encouraging. The pressures and temperatures used were absorption at about 28 atmospheres and 40°F, fractionation at about 3 atmospheres and 127°F, and stripping near 1.3 atmospheres and 87°F. The solvent flow rate was approximately 1 gpm, while the gas feed rate to the absorber column ranged between 5.1

* The three pilot plant columns are filled with Goodloe packing, a product of the Packed Column Corporation, Springfield, New Jersey.

TABLE I

PRELIMINARY ABSORPTION DATA
FROM PILOT PLANT SHAKEDOWN TESTS

Solvent	Refrigerant-11
Temperatures and Pressures:	
Absorber	39 - 42°F; 27 - 28 atmospheres
Fractionator	118 - 137°F; 2.6 - 3.3 atmospheres
Stripper	78 - 96°F; 1.1 - 1.5 atmospheres
Liquid Feed Rate to Absorber	1.0 - 1.1 gpm
Gas Feed Rate to Absorber	5.1 - 6.6 scfm
Absorber L/G Ratio	28 - 48 (weight basis)
Absorber Feed Krypton Concentration	470 - 2740 ppm
Krypton Removal in Absorber	85 - 98% (approximate range)
Stripper Product Flow Rate	0.01 - 0.06 scfm
Krypton Concentration in Stripper Product	1.2 - 7.2%
Oxygen Concentration in Stripper Product	49 - 65%
Overall Process Krypton Concentration Factor:	
Normal	11 - 100
Oxygen-Free Basis	22 - 270

and 6.6 scfm. This choice of gas flow rates was arbitrary, and higher rates have been employed without encountering flooding difficulties.

With krypton concentrations in the absorber gaseous feed stream between 470 and 2,740 ppm, the krypton removal appeared to be satisfactorily high; in these tests, krypton removals of from 85 to 98% were indicated.

The gas product flow rate, i.e., the stripper off-gas rate, was between 0.01 and 0.06 scfm, or approximately two orders of magnitude below the absorber feed rate. The krypton concentrations in the product were between 1.2 and 7.2%, resulting in overall krypton concentration factors of from 11 to 100. Because of the high oxygen content (49 to 65%) of the product stream and its relatively low flow rate, small, inexpensive chemical traps could have been used to remove the product oxygen, thereby increasing the concentration factors by more than a factor of two.

It should be emphasized that the primary purpose of these preliminary tests is to determine system performance and indicate necessary modifications prior to initiating the formal experimental program, rather than to evaluate completely the potential of refrigerant-11 as a process solvent. The fact that krypton concentration factors near 100 have already been observed in some of the tests, however, is encouraging and indicates that further work with this solvent is warranted.

The two major hardware changes suggested by the shakedown test results, i.e., (1) the addition of desiccant traps to the solvent feed system to reduce the possibility of forming ice plugs and to supplement the in-line moisture removal traps already installed as a part of the gas recycle system, and (2) the provision of additional heat transfer surface area on the absorber feed stream, have already been mentioned. Further difficulties, however, have been experienced with some of the temperature and liquid flow instrumentation, and corrective measures are being taken.

In view of the indicated performance of refrigerant-11, the shakedown testing period has been extended somewhat to permit collection of scoping data at different operating conditions, for planning purposes.

CONCEPTUAL DESIGN STUDIES

K. E. Habiger, B. F. Crump

During this report period, a literature survey was made to gather information which might be helpful in estimating the extent of fluorocarbon solvent degradation, due to irradiation, that could be expected in plants using the selective absorption process for krypton and xenon removal.

Only a limited amount of information is available on the radiolytic decomposition of refrigerants-11 and -12, the two solvents of most interest at this time. A series of irradiation tests with uranium-234 alpha

particles was performed using these two compounds by Steidlitz and co-workers at the ORGDP in 1952^[5]. The irradiation results, corrected to 1 atmosphere and 32°F, were presented in the form of average energy utilizations; these values were 26.2 and 27.9 ev/ion pair for refrigerants-11 and -12, respectively. Expressing these results as the more familiar G-values gives 3.82 and 3.58 halogen ions produced per 100 ev of absorbed energy for refrigerants-11 and -12.

The results of irradiation tests using 1.5 Mev electrons and refrigerant-11, conducted at ORNL in 1956, were reported by Silverman, et al^[4]. In these experiments, G-values of 0.62 and 0.16 for the production of chloride and fluoride ions, respectively, were obtained. These tests were carried out at a temperature of minus 94°F, and it was estimated that the reported G-values might increase by an order of magnitude when extrapolated to temperatures near room temperature.

Workers at the du Pont "Freon" Products Laboratory have recently conducted radiolytic decomposition experiments in which various fluorocarbons were exposed to X-rays^[1]. These tests were performed at temperatures from 95 to 100°F; for refrigerant-12, the average G-values observed were about 2.1 for fluoride ions and 1.5 for chloride ions, while for refrigerant-11, the corresponding G-values were 0.9 and 3.7.

It is apparent that the extent of solvent radiolytic decomposition will depend on both the type of radiation involved and temperature conditions, as well as on the magnitude of the solvent dose rates. Furthermore, it should be noted that the dominant radioactive isotope of xenon, xenon-133, which is the most significant contributor to degradation, has a short half-life (5.27 days), and the solvent decomposition rate resulting from its decay will decrease rapidly with cooling time. Thus, the total decomposition rate will approach the krypton value as cooling times extend beyond a few days. Based on a few preliminary calculations made using the available decomposition data, it does not appear that solvent degradation due to irradiation will be high enough to affect system operability for most cases of interest. This problem is being looked at in more detail, however, and estimates of decomposition over a wide range of processing conditions are being prepared.

OPTIMIZATION STUDIES

S. Blumkin, E. von Halle, D. J. Roberts

Work on the preparation and testing of a generalized computer code for use in the optimization studies is now complete. The central part of the code, as mentioned in the previous progress reports, is a mathematical model of the absorption process which can be used to compute vent, recycle, product, and various internal stream flow rates and compositions for a given set of inlet feed conditions and for a set of specified process performance criteria. To this model have been added equipment sizing

and cost estimating routines, so that, for a given separation job, a search can be made for the operating parameters which result in the lowest plant cost.

The first series of case studies using the optimization code was begun recently. These cases, which are keyed to off-gas treatment at a large fuel reprocessing plant, involve a wide range of feed gas flows (20 to 500 scfm), and compositions (20 to 500 ppm krypton, 180 to 4500 ppm xenon), with krypton recoveries near 99%.

STATUS AND FUTURE PLANS

It is expected that the pilot plant shakedown tests will be finished in the near future, and that the formal experimental program, using refrigerant-12 initially, can be begun during the next six months. After the shakedown tests, some system modifications will be made, as already indicated, and equipment insulation will be completed. Also, a gas chromatograph, for continuous monitoring of the compositions of the gaseous process streams, will be installed as soon as possible. This instrument will be used to indicate when steady-state conditions have been achieved, as well as to provide much of the basic performance data required. The conceptual design effort will proceed with further investigation of solvent radiolytic decomposition, and the optimization case studies will be continued.

BIBLIOGRAPHY

- [1] Brock, C. M., "Freon" Products Laboratory, E. I. du Pont de Nemours and Company, Inc., personal communication.
- [2] Merriman, J. R., Pashley, J. H., and Smiley, S. H., Engineering Development of an Absorption Process for the Concentration and Collection of Krypton and Xenon, Summary of Progress through July 1, 1967, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, December 19, 1967 (K-1725).
- [3] Merriman, J. R., and Pashley, J. H., Engineering Development of an Absorption Process for the Concentration and Collection of Krypton and Xenon, Second Summary Progress Report, July through December, 1967, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, August 19, 1968 (K-1745).
- [4] Silverman, M. D., et al, "Radiation Damage to Freon-11, CCl_3F ", Nuc. Sci. Eng., 15, 217 (1963).
- [5] Steidlitz, M. E., et al, "Ionization of Fluorocarbon Gases by U-234 Alpha Particles", J. of Phys. Chem., 56:1010 (1952).